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No. 673

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United States Court of Appeals for the Fourth Circuit.

No. 7298.

SEARS, ROEBUCK AND COMPANY AND
PLYMOUTH RUBBER COMPANY, INC.,
DEFENDANTS, APPELLANTS,

v.

MINNESOTA MINING AND MANUFACTURING
COMPANY,
PLAINTIFF, APPELLEE.

APPEAL FROM THE UNITED STATES DISTRICT COURT FOR THE
MIDDLE DISTRICT OF NORTH CAROLINA.

RECORD APPENDIX TO BRIEF FOR DEFENDANTS, APPELLANTS.

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RECORD APPENDIX.

In the District Court of the United States for the Middle District of North Carolina, Greensboro, Division.

No. 878-G.

MINNESOTA MINING AND MANUFACTURING COMPANY, a Corporation of Delaware, *Plaintiff*,

v.

SEARS, ROEBUCK AND COMPANY, a Corporation of New York, *Defendant*,

and

PLYMOUTH RUBBER COMPANY, INC., *Defendant-Intervenor*.

Findings of Fact and Conclusions of Law.

FINDINGS OF FACT

1. The foregoing identified and numbered suits were consolidated for the purposes of trial by order of this Court dated January 7, 1955.

2. The jurisdiction of this Court is based on the fact that this is a suit arising under the Patent Laws of the United States; and venue is admitted.

3. The several defendants admit plaintiff's ownership of the United States Letters Patent No. 2,559,990 issued to the plaintiff on July 10, 1951, and Reissue Letters Patent No. 23,843 issued to the plaintiff on June 29, 1954, the patent involved in this litigation.

4. Plymouth Rubber Company, Inc., the manufacturer of the most of the accused tape sold by the defendants herein, at the time of the Pretrial conference held in these consolidated cases on September 21, 1955, intervened of

record as defendant-intervenor in No. 878-G, and adopted the Answer and all other pleadings, including Answers to Interrogatories, Answers to Requests for Admissions, and Depositions, heretofore filed in No. 878-G by or on behalf of the defendant Sears, Roebuck and Company.

5. There are involved as accused structures in these consolidated suits, as will appear from other Findings of Fact herein, pressure-sensitive vinyl plastic electrical insulating tape made by two manufacturers and sold by the respective defendants under the brand names indicated, and plasticized as set forth:

Defendant	Manufacturer	Brand Name	Plasticizer	Tape Example
Plymouth Rubber Company, Inc.	Plymouth	Plymouth	Majority production G-40; Minority, G-25	PX 14 DX 32
Sears, Roebuck and Company	Plymouth	Homart	"	PX B-3
Pine State Electric Supply Co., Inc.	Plymouth	S I	"	PX 18
The Noland Company, Inc.	Plymouth	Plymouth	"	PX 15
Scott-Parish Electrical Supply Company	Plymouth	Plymouth	"	PX 14
Dixie Radio Supply Company of Charlotte, Inc.	Plymouth Technical Tape Corp.	Plymouth Tuck	" R-2H & G-60	PX 16 PX 12

6. The defendant-intervenor, Plymouth Rubber Company, Inc., is the manufacturer of the Plymouth Plastic Electrical Tape, charged to infringe.

7. The defendant Sears, Roebuck and Company, prior to the filing of the complaint in 878-G and subsequent to the

grant to the plaintiff of the original of the reissue patent here involved, and continuously thereafter, has sold pressure-sensitive vinyl plastic electrical tape made by Plymouth under the private brand name of "Homart".

8. The defendant Pine State Electric Supply Co., Inc., prior to the filing of the complaint in 879-G and subsequent to the grant to the plaintiff of the original of the reissue patent here involved, has sold vinyl plastic pressure-sensitive electrical tape manufactured by Plymouth Rubber Company, Inc., privately branded "S I" for Superior Insulating Tape Co. of Saint Louis, Missouri, which company sold such tape to said defendant.

9. The defendant Dixie Radio Supply Company of Charlotte, Inc., prior to the filing of the complaint in 879-G and subsequent to the grant to the plaintiff of the original of the reissue patent here involved, has sold Plymouth Plastic Electrical Tape.

10. The defendant Dixie Radio Supply Company of Charlotte, Inc., prior to the filing of the complaint in 879-G and subsequent to the grant to the plaintiff of the original of the reissue patent here involved, has sold No. 330 "Tuck" Vinyl Plastic Insulating Tape manufactured by Technical Tape Corporation of New York.

11. The defendant Scott-Parish Electrical Supply Company, prior to the filing of the complaint in 879-G and subsequent to the grant to the plaintiff of the original of the reissue patent here involved, and continuously thereafter, has sold Plymouth Plastic Electrical Tape.

12. The defendant The Noland Company, Inc., prior to the filing of the complaint in 879-G and subsequent to the grant to the plaintiff of the original of the reissue patent here involved, and continuously thereafter, has sold Plymouth Plastic Electrical Tape.

13. The plaintiff in its charge of infringement relies on claims 1, 3, 4, 6, 7, 8 and 9 of its Reissue Patent No. 23,843.

Of these claims, numbers 1, 3 (except for correction of temperature and 4 are identical with similarly numbered claims of the original patent; and claims 6, 7, 8 and 9 are reissue claims. Of the claims in issue, claims 1 and 6 may be taken as typical.

14. Over 90% of Plymouth's sales from the date of issue of the original patent to October 3, 1955 of pressure-sensitive vinyl plastic insulating tape (other than to the government and agencies thereof) has been of such tape made using a plasticizing material other than G-25. The majority of the Plymouth tape charged to infringe has been made using Paraplex G-40 as the plasticizing material for the vinyl film backing.

15. Plymouth first sold pressure-sensitive vinyl plastic insulating tape containing recent-vintage Paraplex G-25 as the plasticizer in the tape backing (other than to the government or an agency thereof) on or about June 24, 1954. This sale was to Sears, Roebuck and Company.

16. The plaintiff's pressure-sensitive plastic electrical insulating tapes, for example "SCOTCH" brand No. 33 and No. 22 Electrical Tapes, are made in accordance with teachings of the patent in suit.

17. The plaintiff's tapes made under the teachings of the patent in suit met with an immediate commercial success due to their inherent merit. Plaintiff's sales, following the first small sale in February 1945, rose from about $8,000.00 in 1945 to more than $8,000,000.00 in 1953, with an advertising expense over the period of less than 2% of sales.

18. In one of its principal uses, as an electrical splicing tape, the tape of the patent in suit replaces both rubber electricians' tape and friction tape. The two manufacturers of the tape here accused truthfully so represent to the trade, as do the defendant sellers.

19. Prior to the invention by the patentees of the tape of the patent in suit, tape of such kind did not exist. The in-

vention of the patent in suit provided a tape which was an entirely new article of commerce, different in character and kind from anything which preceded it.

20. It was not for want of available materials that the tape of the invention of the patent in suit was not produced earlier. The evidence discloses that the ingredients needed for the formation of the film backing of the tape, as well as those needed for the adhesive and primer, were known in the art and available commercially for a long time, more than ten years, anterior to the invention of the subject matter of the patent in suit.

21. A ready market existed for the tape of the patent in suit many years before it appeared.

22. When these suits were filed, the tape of a third manufacturer was involved, Van Cleef Bros., a division of Johns-Manville Corporation. That manufacturer acquired a license under the patent in suit as of August 30, 1955. Its royalty payment for the first month under the license was $6,243.00, calculated at 5% of sales.

23. The "Homart" plastic tapes made and packaged for the defendant Sears, Roebuck and Company, more recently by Plymouth Rubber Company and earlier by Van Cleef Bros. Co., a division of Johns-Manville Corporation, via Accurate Manufacturing Company, were similar. Both were pressure-sensitive, stretchable and retractable vinyl plastic insulating tapes, similarly advertised and sold and employed for similar uses, and indistinguishable from each other except for a coding or marking on the containers thereof.

24. The patent in suit exhibits invention of a high order. It took the chief chemist of Plymouth Rubber Company, Inc., under mandate of his superiors, from 1948 to 1950 to duplicate the tape of the patent, with the plaintiff's product before him, even though he was experienced in vinyl resins

and the use of plasticizers, and was familiar with the published specifications of plaintiff's No. 33 plastic tape.

25. The accused tapes are not distinguishable in appearance from plaintiff's tape except by examination of labels.

26. Others tried, without success, to make a pressure-sensitive tape on a plasticized vinyl film backing. Tierney tried in 1938, but all attempts were unsatisfactory and the pressure-sensitive adhesives became very soft and pasty. Another employee of plaintiff tried in 1941, but met with failure and abandoned the project.

27. The inventors, prior to the production of the successful tape as disclosed by the patent in suit, collaborated for many months in experimental work, during the course of which a series of over 200 experiments was conducted with a large number of different formulations.

28. None of the five items of prior art ultimately relied upon by the defendants (selected from an initial citation of over 25) discloses the tape of the patent in suit. At most, taken separately, each discloses the antiquity of an element or ingredient of the article of the patent. No one of these patents teaches, or even remotely suggests, how to produce the tape of the Oace patent. The prior art relied upon is even less pertinent than the Schmidt patent No. 2,332,265, which was a file wrapper reference, and which was first pleaded, and was then withdrawn by defendants during the trial. The prior art relied on at the trial is as follows:

Groff	No. 1,966,856
Drew	No. 2,177,627
Maibauer	No. 2,320,442
Sears	No. 2,413,673
Bierbrauer	No. 206,871 (Swiss)

29. The subject matter of the Oace et al patent in suit is an electrical insulating tape in the form of a relatively thin (about 4 to 20 mils) backing film, which is easily stretchable

(by simple hand pulling) and readily retractable, combined with a well bonded water-insoluble, normally tacky and pressure-sensitive adhesive coating, the backing film being formed from a plasticized vinyl chloride polymer which is in permanent equilibrium with the adhesive coating in order that the adhesive will not soften (become pasty) or lose tack (become non-adherent), thereby providing an insulating tape that may be wound in a roll and unwound therefrom without delamination of the tape or offsetting of the adhesive.

30. The central problem to which the patent in suit is addressed, and which it solved, was to provide an insulating tape in the form of an easily stretchable and highly elastic pressure-sensitive adhesive tape comprising a well-bonded, water-insoluble, non-corrosive, normally tacky and pressure-sensitive coating on a plasticized vinyl chloride polymer film which is in permanent equilibrium with the adhesive.

31. The patent in suit teaches persons skilled in the art that ethyl acrylate polymer may be used as the plasticizer for the film backing of the tape of the patent. The patent discloses a plasticizing system which is satisfied by one or more ingredients of plasticizing material. There is in evidence a roll of pressure-sensitive insulating tape wherein the film backing is 100 parts of VYNS vinyl chloride copolymer resin plasticized with 50 parts by weight of ethyl acrylate polymer resin.

32. The Oace reissue specification introduced no new matter over the specification of the original Oace patent. The only changes in the reissue patent specification from the specification of the original patent are the italicized portions appearing in columns 1, 8 and 9. None of the added portions makes a new disclosure of invention but rather are merely further discussions of the advantages claimed for this type of tape, or definitions.

33. Each of the claims in suit particularly points out and distinctly claims the invention disclosed in the patent in suit.

34. The reissue patent is for the same invention as the original patent. There is no change in disclosure; and the claims of the reissue comprehend no more than the inventors disclosed and intended to cover originally.

35. The original Oace patent was partly inoperative clearly and distinctly to cover, in literal terms, the inventions disclosed therein and intended to be claimed. This defect arose through error, and without any deceptive intention.

36. Lack of patent experience on the part of the applicants (Oace et al), and lack of understanding of the invention on the part of their patent solicitors constituted error justifying the Patent Office in its grant of the clarifying reissue.

37. Plasticization and migration are both physical phenomena.

38. Paraplex G-25 and Paraplex G-40 are respectively the polymerized reaction products of sebacic and adipic acid with a dihydric alcohol; and each is a soft, viscous linear polyester alkyd plasticizer resin.

39. In the process of polymerization, the composition of the resultant product depends upon the conditions of the polymerization, for example, time, temperature, the catalyst employed, and other factors, so that different types of polymers can be produced as desired.

40. Paraplex G-25 and Paraplex G-40 are represented by the manufacturer thereof to be "tailor-made", and to combine to a marked degree many of the desirable features of the more liquid ester-type plasticizers, such as dioctyl phthalate, with those features obtainable in resinous plasticizers.

41. Paraplex G-25 is represented by its manufacturer to be "a soft, tacky, viscous liquid which pours slowly at room temperature". Paraplex G-40 has even a lower viscosity than Paraplex G-25 at "slightly elevated temperatures".

42. Polyester plasticizers for vinyl chloride copolymers, such as Paraplex G-25 and Paraplex G-40 made by Rohm & Haas, may be fractionated by known procedures, but not by distillation, into the more viscous higher-molecular-weight portions and the more liquid lower-molecular-weight portions of the original material.

43. The more liquid portion of Paraplex G-40 is a liquid adipyl ester plasticizer. Both adipyl ester plasticizers and phthalyl ester plasticizers are plasticizers for vinyl chloride polymers; both are esters of organic carboxylic acids; both are liquid; and both are non-volatile.

44. Sebacic, adipic and phthalic acid esters are available as liquid plasticizers for vinyl chloride polymers, offered in commerce, and referred to in the literature in the same grouping; and all function by physical action in the same way to produce soft, pliable, stretchable and elastic polyvinyl chloride film.

45. When the lower-molecular-weight fraction of Paraplex G-40 is blended with the more viscous higher-molecular-weight portion, a plasticizer is obtained which, by physical action in combination with vinyl chloride polymers, functions in the same way to give essentially the same results as the combination of Paraplex G-25 and dioctyl phthalate in the ration of 2 to 1.

46. The more liquid lower-molecular-weight portion of Paraplex G-40 constitutes about 33% thereof. This portion is a liquid adipyl ester plasticizer; and is the equivalent of a liquid phthalyl ester plasticizer. The ratio of two parts of higher-molecular-weight viscous resinous plasticizer to one part of more liquid lower-molecular-weight plasticizer found in Paraplex G-40 is within the recommended range

of examples of the Oace patent. The use of Paraplex G-40 as the plasticizing material in the accused Plymouth tapes produces the same results in the same way by the same or equivalent means as the examples of the patent in suit.

47. A person skilled in the art can produce the tape as disclosed by the Oace patent by following the teachings of the patent. Plaintiff's commercial tape is made in accordance with the teachings of the patent. The accused tape was not derived from the prior art; rather it was produced by Plymouth and Technical Tape, respectively, essentially by duplicating plaintiff's commercial tape.

48. The purpose of vacuum stripping during the manufacture of Paraplex G-25 and Paraplex G-40 by Rohm & Haas is to remove free glycol and water which may result from the poly-esterification, and does not remove ester material of the order of 300, 400 or 500 molecular weight. The building unit, or monomer, of both G-25 and G-40 has a molecular weight falling within the range of about 300-350.

49. Paraplex G-25, when the applicants for the patent in suit worked with it in 1944 and 1945, was significantly different than it is today.

A. The attempt of Oace et al in 1944 to make their tape with Paraplex G-25 as the sole plasticizer led to a tape which was unsuccessful and quickly lost its tack.

B. Danovitch of Plymouth could not make tape with G-25 as the sole plasticizer in the period from 1948-1950.

C. In late 1943 and 1944, Paraplex G-25 was in the process of development for manufacture on both a pilot-plant and plant scale. Its composition by that time had been defined research-wise "at least in respect to its major features". The first production batch of Paraplex G-25 was not made until early 1944.

D. In the production of Paraplex G-25 in recent years, Rohm & Haas, the manufacturer, has held the product to narrower specifications.

E. Paraplex G-25, like other polymerized plasticizers, can be tailored by process controls, and is so tailored, to get desired results to meet customers' demands.

F. Paraplex G-25 of recent vintage as the sole plasticizer will make suitable tape today, although still not as good as when some additional low molecular weight plasticizer is used.

G. Paraplex G-25 of 1944 and 1945 vintage had an oil film on its surface in the containers; recent vintage Paraplex G-25 does not have an oil film.

H. Paraplex G-25 is not a chemically-pure compound, even today.

50. The use of Paraplex G-25 of recent vintage as the plasticizer material in the film backing makes a tape of satisfactory aging life, fully responsive to the disclosure of the patent, although there is a relatively low amount of tack loss. The quality of such tape is improved when a small amount of a more liquid plasticizer, such as dioctyl phthalate, is added to the plasticizer material.

51. The more liquid lower-molecular-weight portion of the recent vintage Paraplex G-25 constitutes about 11% thereof. This portion is a liquid sebacyl ester plasticizer. The ratio of about 8 or 9 parts of higher-molecular-weight viscous alkyd resin plasticizer to about 1 part of more liquid lower-molecular-weight plasticizer found in this Paraplex G-25 is within the compass and scope of the Oace patent. The use of Paraplex G-25 as the plasticizing material in the accused Plymouth tapes produces the same results in the same way by the same or equivalent means as the examples of the patent in suit.

52. The plasticizing materials herein found to be full equivalents for those specifically recited ingredients disclosed in the patent in suit are either tailor-made for the purpose or are normal, well-known substitution products for the material specified in the patent, and which would be used by persons skilled in the art without experimentation.

53. The accused Plymouth Plastic Electrical Tape which utilizes Paraplex G-40 as the plasticizing material, made and sold by the defendant Plymouth Rubber Company, Inc., and sold by defendants in these consolidated cases, responds to all of the requirements of each of claims 1, 3, 4, 6, 7, 8 and 9 of reissue patent in suit, and infringes each of said claims.

54. The accused Plymouth Plastic Electrical Tape which utilizes Paraplex G-25 as the plasticizing material, made and sold by the defendant Plymouth Rubber Company, Inc., and sold by the defendant Sears, Roebuck and Company, responds to all of the requirements of each of claims 1, 3, 4, 6, 7, 8 and 9 of the reissue patent in suit, and infringes each of said claims.

55. The defendant Plymouth Rubber Company, Inc., uses the same equipment for mixing, milling, calendering and coating the accused tapes that is used in the manufacture or processing of other articles before the issue of the original of the patent in suit. The evidence shows that the manufacture and sale of the accused tape by Plymouth was initiated, using existing equipment and existing sales force, in order to protect its business in the manufacture and sale of rubber electricians' tape and friction tape. None of the defendants has offered any evidence that any substantial preparation was made for the purpose of manufacturing or selling the accused tape.

56. The defendant Plymouth Rubber Company, Inc., commenced the manufacture and sale of the accused tape late in 1950.

57. The defendant Plymouth Rubber Company, Inc., has failed to establish any facts to support laches or inequity on the part of the plaintiff to deny relief to the plaintiff. The taking out of insurance by Plymouth and its seeking the advice of patent attorneys was not communicated to the plaintiff. A report of patent counsel was concealed from the plaintiff, after inquiry, until this trial was in its last day.

58. Plaintiff was not guilty of laches or inequity either in the filing or prosecution of the Oace reissue application, or in the commencement of the instant actions.

59. The "Tuck" Vinyl Plastic Insulating Tape sold by the defendant Dixie Radio Supply Company of Charlotte, Inc., and made by Technical Tape Corporation of New York, comprised a copolymer of vinyl chloride and vinyl acetate plasticized with R-2H and Paraplex G-60.

60. R-2H is a viscous, non-migrating alkyd plasticizer resin of the polyester type, like Paraplex G-25 and Paraplex G-40. It is liquid, fluid and viscous. It is marketed by Carbide & Carbon Chemical Corporation.

61. Paraplex G-60 is a liquid ester plasticizer made by Rohm & Haas for plasticizing vinyl chloride. Its number average molecular weight is 1000, compared with 390 for dioctyl phthalate, 6000 for Paraplex G-40, and 8000 for Paraplex G-25.

62. Paraplex G-60 and R-2H are respectively the equivalents of dioctyl phthalate and Paraplex G-25. It would be logical for a man skilled in the art of plasticizing vinyl chloride resins to substitute Paraplex G-60 for dioctyl phthalate; and R-2H for Paraplex G-25, both being viscous low-acid-number alkyd plasticizer resins. He would expect to get the same results in the same way by using the same or equivalent means, and would get the same results, as shown by Plaintiff's Exhibit 12 herein.

63. The "Tuck" vinyl plastic insulating tape sold by the defendant Dixie Radio Supply Company of Charlotte, Inc., and manufactured by Technical Tape Corporation of New York, responds to all of the requirements of each of claims 1, 3, 4, 6, 7, 8 and 9 of the reissue patent in suit.

64. Each of the defendants herein by its acts and conduct of infringement has and does threaten to continue to infringe.

Conclusions of Law

1. The Court has jurisdiction of the subject matter of these suits and of the parties thereto.

2. The original Oace et al patent No. 2,550,990 was in all respects duly and lawfully reissued as Reissue No. 23,843.

3. Claims 1, 3, 4, 6, 7, 8 and 9 of the Oace Reissue patent No. 23-843, all of the claims in issue, are each valid.

4. Each of the aforesaid claims 1, 3, 4, 6, 7, 8 and 9 of said reissue patent has been infringed by the defendant-intervenor Plymouth Rubber Company, Inc., in the manufacture, use, sale, and offer for sale of Plymouth Plastic Electrical Tape, "Homart" Plastic Electrical Tape, and "S I" Plastic Electrical Tape, each being a pressure-sensitive adhesive insulating tape having a backing of vinyl chloride polymer plasticized with Paraplex G-40 or Paraplex G-25.

5. Each of the aforesaid claims 1, 3, 4, 6, 7, 8 and 9 of said reissue patent has been infringed by defendant Sears, Roebuck and Company in the use, sale and offer for sale of "Homart" Plastic Electrical Tape made by Plymouth Rubber Company, Inc.

6. Each of the aforesaid claims 1, 3, 4, 6, 7, 8 and 9 of said reissue patent has been infringed by the defendant Scott-Parish Electrical Supply Company and The Noland

Company, Inc., in the use, sale, and offer for sale of Plymouth Plastic Electrical Tape.

7. Each of claims 1, 3 and 4 of said reissue patent has been infringed by the defendant Pine State Electrical Supply Co., Inc., in the use, sale, and offer for sale prior to June 29, 1954 of "S I" Plastic Electrical Tape made by Plymouth Rubber Company, Inc.

8. Each of claims 1, 3 and 4 of said reissue patent has been infringed by the defendant Dixie Radio Supply Company of Charlotte, Inc., in the use, sale, and offer for sale prior to June 29, 1954 of (a) Plymouth Plastic Electrical Tape and (b) "Tuck" Vinyl Plastic Insulating Tape, the latter made by Technical Tape Corp., New York City.

9. The plaintiff has not been guilty of any inequity, laches, or estoppel to deny it full relief; and no defendant has acquired any intervening right.

10. The plaintiff is entitled to a decree providing for (1) a permanent injunction against each defendant and the defendant-intervenor prohibiting further infringing acts, (2) damages against each defendant and the defendant-intervenor; and (3) costs.

The Court finds the facts and makes the conclusions of law which are tendered by the plaintiff, as hereinabove set forth, and a decree shall be entered in accordance with said findings of fact and conclusions of law.

This the 12 day of June, 1956.

JOHNSON J. HAYES
United States Judge.

Decree.

THIS CAUSE came on to be tried before the Court, sitting without the intervention of a jury, and the Court having

considered the evidence introduced by the parties, including stipulations, exhibits, and the entire record in the cause, as well as the briefs and arguments of counsel for the respective parties; and the Court having heretofore made and filed its findings of fact and conclusions of law, as the same appear of record, which are made a part hereof by reference thereto;

IT IS, THEREFORE, ORDERED, ADJUDGED AND DECREED as follows:

(1) That United States Letters Patent No. 2,559,990 was duly and lawfully issued to the plaintiff on July 10, 1951, and was in all respects duly and lawfully reissued to the plaintiff on June 29, 1954 as Reissue No. 23,843; and that the plaintiff is the sole and exclusive owner of the full and entire right, title and interest in and to said Letters Patent and the reissue thereof, together with all rights of action for past infringement thereof;

(2) That said Reissue Patent No. 23,843 is good and valid in law as to claims 1, 3, 4, 6, 7, 8 and 9, all of the claims in issue herein;

(3) That the defendant-intervenor, Plymouth Rubber Company, Inc., has infringed each of the aforesaid claims 1, 3, 4, 6, 7, 8 and 9 of said reissue patent by the manufacture, use, sale and offer for sale of pressure-sensitive stretchable and retractable plastic tape, designated as "Plymouth" Plastic Electrical Tape, "Homart" Plastic Electrical Tape and "S I" Plastic Electrical Tape, and illustrated by Plaintiff's Exhibits 14, 15, 16, 18 and B-3 and by Defendants' Exhibit 32;

(4) That the defendant, Sears, Roebuck and Company, has infringed each of the aforesaid claims 1, 3, 4, 6, 7, 8 and 9 of said reissue patent by the use, sale and offer for sale of pressure-sensitive stretchable and retractable plastic tape, designated as "Homart" Plastic Electrical Tape, made by Plymouth Rubber Company, Inc., and illustrated

by Plaintiff's Exhibits 14, 15, 16, 18 and B-3, and by Defendants' Exhibit 32;

(5) That a writ of injunction issue out of and under the seal of this Court, directed to the defendant, Sears, Roebuck and Company, and to the defendant-intervenor, Plymouth Rubber Company, Inc., perpetually restraining and enjoining them and each of them, and each of their directors, officers, associates, agents, attorneys, confederates and employees, and those in active concert or participating with them or either of them, from directly or indirectly making, selling, offering for sale, using, or causing to be made, sold or used, any adhesive sheeting or adhesive tape the same as the adhesive sheets or adhesive tapes identified as Plaintiff's Exhibits 14, 15, 16, 18 and B-3, and by Defendants' Exhibit 32, or any other pressure-sensitive stretchable and retractable plastic tape or any device utilizing or embodying the inventions of claims 1, 3, 4, ~~6, 7~~, 8 and 9 of said Letters Patent Reissue No. 23,843; or from in any manner infringing upon any of said claims of such Letters Patent;

(6) That the plaintiff, Minnesota Mining and Manufacturing Company, shall have and recover of the defendant-intervenor, Plymouth Rubber Company, Inc., the damages which the plaintiff has sustained by reason of the aforesaid infringements by said defendant-intervenor;

(7) That the plaintiff, Minnesota Mining and Manufacturing Company, shall have and recover of the defendant, Sears, Roebuck and Company, the damages which the plaintiff has sustained by reason of the aforesaid infringements by said defendant;

(8) That this cause shall be referred to Rufus Reynolds, Esquire, as Special Master, to ascertain the damages adequate to compensate the plaintiff for the several infringements by the defendant, Sears, Roebuck and Company, and by the defendant-intervenor, Plymouth Rubber Company, Inc.; and

(9) That the plaintiff recover of the defendant and the defendant-intervenor the taxable costs of the plaintiff in this suit, and such costs and expenses as may be incurred by the Special Master in connection with his services herein, and that the plaintiff shall have judgment and execution against the said defendants for said costs.

Entered this 12 day of June, 1956.

JOHNSON J. HAYES
United States District Judge.

Opinion.

[June 4, 1956.]

HAYES, District Judge.

This infringement suit is brought by the assignee of a patent on a pressure-sensitive stretchable and retractable vinyl plastic tape primarily for use as an electrical insulating tape. The original application was filed by Oace, Snell and Eastwold January 12, 1946 and Patent 2,559,990 issued July 10, 1951, naming them as assignors to the Minnesota Mining and Manufacturing Co. For convenience it will be referred to as the Oace Patent. Also involved is Reissue Patent 23,843 of June 29, 1954, on application filed July 9, 1952. All available defenses are asserted.

Prior to the Oace invention, great difficulties with conventional methods of splicing electric conductors had been encountered, among others, the bulky and cumbersome and time consuming element in making splices; the materials available were ineffective under temperature changes of heat and moisture; the loss of tackiness (adhesiveness) and by becoming soft and pasty, resulting, in the tape then in use, in loosening and becoming ineffective. Slight increases in temperature above normal room temperature increased this tendency to impair the effectiveness of the splicing

material with the consequent grave hazards of escaping voltage.

The Oace invention overcame these and other defects by providing an insulated spliced electrical conductor which is "electrically, mechanically and chemically effective" and is readily and quickly prepared without use of special procedures or equipment. These results were obtained by the use of an insulating tape in the form of a relatively thick but easily stretchable and highly elastic pressure-sensitive adhesive tape comprising a well-bonded, water-insoluble, non-corrosive, normally tacky and pressure-sensitive adhesive coating on a plasticized vinyl chloride polymer film which is in permanent equilibrium with the adhesive; it neither softens nor loses its adhering qualities on prolonged contact with the backing or film layer.

Oace found that high molecular weight modifier such as "Paraplex G-25" would produce the desired strength, stretch and elasticity in vinyl chloride polymer films, though classed as "non migrating" or "permanent" plasticizers, failed to provide for permanent equilibrium of adhesive and backing. When tape made in that manner was unwound from the roll, after a moderate period of storage it would not adhere either to the electrical conductor or to its own backing, and was of no value as an insulating and protective coating. Oace provided an electrical insulating tape having stretch and elasticity rendering it highly effective for wrapping wire and cable splices. It was stretchable to the extent of 50% at room temperature, by mere pulling with the hands; it could be stretched 30% at room temperature and would retract to substantially its original length. He discovered how to overcome moisture and temperature destruction and to prevent loss of adhesiveness due to migration. He gave examples of insulating tapes in the form of pressure-sensitive adhesive tapes having a vinyl polymer film base prepared with a vinyl chloride vinyl

acetate copolymer softening at about 280 degrees F. and in the ratio of vinyl chloride to vinyl acetates of approximately 89:11. After giving many examples, he finds that the plasticizer must be compatible with the vinyl polymer, and must be sufficiently low in volatility so that it is not driven off during milling and calendering, or during subsequent storage and use.

After citing five examples of the various embodiments of his invention, for purposes of illustration rather than limitation, he makes the five claims set out in the margin.[1]

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1. 1. A pressure-sensitive adhesive insulating tape wound upon itself in roll form and comprised of: a stretchable and elastic film backing having a thickness of 4 to 20 mils and formed of a homogeneous mixture primarily consisting of a stable blend of a film-forming polymer of monomers including at least a major proportion of vinyl chloride, a substantially non-volatile liquid phthalyl ester plasticizer amounting to 8 to 20 parts per 100 parts of said polymer, and a soft and viscous low-acid number alkyd plasticizer resin in amount at least equal to the amount of said liquid phthalyl ester plasticizer, the total amount of said plasticizers about being ⅓ to ½ the amount of said polymer and the proportions being such that the adhesive tape has the properties of stretch and elasticity hereafter specified without causing pastiness or tack-loss of the contracting adhesive in the roll; and a eucohesive normally tacky and pressure-sensitive rubber-resin type adhesive coating united to the inner face of said film backing; said adhesive tape being unwindable without delamination or offsetting of adhesive, being originally stretchable by hand-pulling to an extent of at least 50% at room temperature and being substantially completely retractable from an elongation of 30% as herein specified.

2. An adhesive tape according to claim 1, wherein the adhesive includes a small proportion of an oil-soluble heat-reactive phenol-aldehyde resin.

3. An adhesive tape according to claim 1 in which the film forming polymer is a copolymer of vinyl chloride and a minor proportion of vinyl acetate, said copolymer having a softening temperature of at least about 280 degrees C.

4. A pressure sensitive adhesive insulating tape wound upon itself in roll form and comprised of: (1) a stretchable and elastic film backing having a thickness of 4 to 10 mils and formed of a homogeneous mixture primarily consisting of a stable blend of

The reissue copies all contained in the original patent, and adds claims 6, 7, 8, and 9 to the five of the original patent. Claim 6 typical of the others is cited in the margin.[2]

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70 parts of a copolymer of vinyl chloride and a minor proportion of vinyl acetate, about 10 parts of a substantially non-volatile liquid phthalyl ester plasticizer, and about 20 parts of a soft and viscous low-acid-number alkyd plasticizer resin; (2) an adhesive primer coating on the inside face of the film backing adapted to increase the anchorage of the adhesive coating; and (3) a eucohesive normally tacky and pressure sensitive rubber-resin type adhesive coating bonded to said primer coating; and said adhesive tape being unwindable without delamination or offsetting of adhesive being originally stretchable to an extent of at least 100% at room temperature and being substantially completely retractable from an elongation of 30% as herein specified.

5. An adhesive tape according to claim 4, wherein the adhesive includes a small proportion of an oil-soluble heat-reactive phenol-aldehyde resin.

2. 6. A pressure-sensitive adhesive insulating tape wound upon itself in roll form and comprising: (1) a water-insoluble and hydrocarbon-oil-insoluble film backing of high dielectric strength containing a stabilizer and having a thickness of 4-20 mils and formed of a homogeneous mixture primarily consisting of a stable blend of (a) a film-forming polymer of monomers including at least a major proportion of vinyl chloride, and (b) a substantially non-volatile plasticizing material therefor in an amount within the range of at least ⅓ the weight of said polymer but in a substantially lesser amount than said polymer and comprising at least a major proportion of a non-migrating viscous plasticizer resin, and the proportions being such that the adhesive tape has the properties of stretch, elasticity and retractability hereafter specified without causing pastiness or loss of the tack of the contracting adhesive in the roll; (2) an adhesive primer coating on the inner face of the film backing adapted to increase the anchorage of the adhesive coating; and (3) a water-insoluble normally tacky and pressure-sensitive rubber-resin type adhesive coating united to the inner face of said film backing, over said primer coating, said adhesive coating being thin in relation to said film backing; said film backing being in permanent equilibrium to said pressure-sensitive adhesive coating so as to avoid pastiness or loss of tack of the said adhesive coating and diminution of the flexibility of said film backing; said adhesive tape being unwindable from the roll without delamination of the tape or

The specification of the reissue is the same as the original patent except comment on the novelty of the tape and definition of terms. There are no additional disclosures of a tape or how to make it. The claims of the reissue appear to embody nothing not disclosed in the original application and invention and they do not broaden the disclosures of the original patent that are further descriptive or illustrative of the teachings of the original patent. The recent case in the Fourth Circuit of Florence-Mayo Nuway Co. v. Hardy, 168 F.2d 778, appears to state the principles of law applicable to the instant case. Applying the principles of law so ably stated by Judge Parker in Colgate-Palmolive Co. v. Carter Products, Inc., 4 Cir., 230 F.2d 855, to the facts in this case, we conclude that the patent is valid. The instant case and the Palmolive case above are not in conflict with the opinion in Sinclair & Carroll Co. v. Interchemical Corp., 325 U.S. 327, 65 S.Ct. 1143, 89 L.Ed. 1644.

Much of the controversy here arises from the employment of Paraplex G-25 as one of the ingredients in the production of the tape by the plaintiff and by the defendants in the accused tapes.

It is perfectly clear that the Paraplex G-25, when the application for the original patent was filed, was of a substantially different formula than that of its later or subsequent vintage. This old formula of Paraplex G-25, in part, accounted for the defects of the tape which became manifest from the exposure, change of moisture or temperature or

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offsetting of the adhesive, being originally stretchable in widths not greater than about one inch by simple hand pulling, exercising a force of not more than about 10 to 15 pounds, to an extent of at least 50% at room temperature and being substantially completely retractable from an elongation of 30%, as herein specified; said tape being readily conformable to irregular surfaces in insulating wire splices and its elasticity, retractability and high adhesion value making it easy, in insulated splices, to produce snug wrappings and coverings, and said tape having sufficiently aggressive adhesiveness to remain tightly and snugly wrapped around splices and wires.

from storage. The problem was to discover what to do to solve these difficulties. Oace discovered and taught how Paraplex G-25 could not be used alone but the combinations with it which would add to the equilibrium of the tape and vastly prolong its usefulness and efficiency, and how to eliminate migration. The evidence abundantly shows that the subsequent vintage of Paraplex G-25 was altered and tailored so that, in a large measure, it overcame the migration. But the alteration of Paraplex G-25 which in its new vintage included the old vintage of Paraplex G-25 and the chemical product which plaintiffs discovered necessary to use in combination to solve the problem, does not invalidate the patent or excuse the defendants from infringement.

If it be granted that there was novelty in the chemical combination which resulted in a non-migrating adhesive tape which was resistant to changes of heat and moisture and storage, and if we conclude, as the evidence shows, that such a solution was discovered by using dioctyl phthalate or other plasticizer compatable with vinyl polymer and with a definite ratio which was sufficiently low in volatility so that it was not driven off during milling, storage or from exposure; and the desired film could be produced from a mixture of 700 parts of Vinylite VYNS, 200 parts of Paraplex G-25, 100 parts of dioctyl phthalate and 25 parts calcium stearate milled together and calendered to a thickness of 4 mils; to which was added a primer made of 965 lbs. of an ammoniacal casein with 624 lbs. of an aqueous dispersion containing 38% by weight of a copolymer of 50 parts butadiene and 50 parts styrene after drying resulted in an extremely thin primer film then add to the primed film the mixture of properly apportioned elements constituting the pressure-sensitive adhesive, the three elements —film, primer and adhesive—, resulting in the new combination for making the desired tape as is taught in the Oace Patent, then it is obvious that a subsequent alteration

of some of these elements, for example, by including two of them into one element, and thereafter using the result, could not invalidate the patent nor successfully avoid infringement. Judge L. Hand in Royal Typewriter Co. v. Remington Rand, 2 Cir., 168 F.2d 691, 693, tersely stated the principle in these words: "Courts have with curious unanimity held that it does not avoid infringement to combine into one member that which the patent discloses as two, if the single member performs the duties of both in the same way."

The accused tapes clearly infringe claims 1 of the original patent and 6 of the Re-issue. Not only are the accused tapes the equivalent of the tape embodied in the above claims but they are practically identical in result. Moreover, they actually embody the very chemical equivalents taught in both the original patent and in the Re-issue. It is significant that Plymouth discounted the value and marketability of plaintiff's product until it became the leader in the electric tape field. Plymouth's salesman discovered this and afterwards Plymouth came out with the accused tapes. In August, 1947, General Electric, speaking of No. 33 Scotch electrical tape (under Oace Patent), said: "For the first time in fifty years a revolutionary electrical tape is on the market ready for immediate delivery."

The commercial success of the patented tape was phenominal. In 1945 t[illegible] sales were $8,270.19; in 1946, $94,000; in 1948, $1,500,000 and in 1953 reached $8,712,744.75. When Plymouth copied Oace Patent, its sales jumped rapidly to $400,000 in 1952 and $500,000 in 1953. In 1950 and 1951, Plymouth's output was so small it did not bother to get the figures.

A decree will be entered permanently enjoining each defendant from further infringement and appointing Rufus Reynolds, Esq., to ascertain the damages.

Excerpts from Discovery Depositions of Louis Klein, E. M. Beavers, Arthur L. Blount and John Myers, Taken by Defendant at Philadelphia, March 22-23, 1955.

Deposition of LOUIS KLEIN, witness called by defendant, Vice-President in charge of sales of Resonance Products Division, Rohm & Haas Company:

Direct Examination.

. . . . . .

[4] Q5. In this case there has been mentioned from time to time a certain plasticizer called Paraplex G-25. Are you familiar with that plasticizer? A. Yes, I certainly know about it. It was an im- [5] portant product in the Resinous Products & Chemical Company.

. . . . . .

[8] Q18. Now, Mr. Klein, was there any, shall we say, principal use of this plasticizer almost at the outset of your manufacture thereof? [9] A. Yes. I don't recall the early history of AR-148 as such when the product was known under that designation, but in the case of Paraplex G-25, the first important commercial use was in a vinyl sheathing for specialized electrical application.

Q19. That was the government use on the polyethylene cable? A. It was the government use on the polyethylene cable.

. . . . . .

Q22. That was the so-called coax radar cable, in which the government was interested at that time? A. The radar cable is what we knew it as. I recall that so well because it was such an important use, because there was an important problem to solve and this solved it.

Q23. A vital government need at that time? A. Very vital.

. . . . . .

[39] Q104. I call your attention to the letter of October 26, 1943 and ask you if it does not consider the use of AR-148, that is, G-25, in connection with a monomeric [40] plasticizer. A. This letter of October 26, 1943 says that we were at that time planning to consider the use of Paraplex AR-148 (G-25) together with an ester-type plasticizer, and by that we meant monomeric.

Q105. A monomeric plasticizer? A. Monomeric plasticizer.

. . . . . .

[66] Q155. Returning again to Defendants' Exhibit 24 for identification, and particularly the last paragraph on numbered page 2 thereof, under the heading "Paraplex G-25,"—do you have a copy in front of you? A. Yes.

Q156. Do you there find a reference to the use of Paraplex G-25 with other plasticizers as a general statement? A. I interpret this paragraph to mean that in commercial practice it is customary to use more than one plasticizer with the vinyl resins, meaning that is what is customarily used—not that it is necessary to use more than one plasticizer.

. . . . . .

Cross-Examination.

[72] XQ180. Yes, I see. But there are some differences in [73] molecular weight or viscosity between Paraplex G-20 and Paraplex G-25, are there not? A. Well, there is in our opinion a real difference in the nature of G-25 and G-20. We characterize G-25 as a linear polyester. Paraplex G-20 is not a linear polyester.

. . . . . .

[90] XQ238. Do you know what G-20 was sold and produced for during the early thirties, the '30 to '35 period? A. Yes, sir, I do.

XQ239. And the major thing was what? I mean, the [91] general type of use. A. Well, plasticizing nitrocellulose.

. . . . . .

[92] XQ247. That isn't quite my question, Mr. Klein. I am not suggesting that you pushed it for that purpose. My question was whether you mean your testimony to be that your company had Paraplex G-20 on the market from 1929 to 1944 without even realizing that it was compatible with vinyl chloride polymers. A. Well, I don't know how to answer that question. Just in my mind it doesn't stick that Paraplex G-20 was commercially useful with vinyl chloride copolymers.

XQ248. Is it today useful with vinyl chloride copolymers? [93] A. Not to my knowledge.

. . . . . .

[129] XQ376. Is G-25 chemically the same material today as when it was first offered commercially by your company? A. To the best of my knowledge it is.

XQ377. Is G-20 the same today as when it was first offered commercially? A. Again, to the best of my knowledge it is.

. . . . . .

[141] XQ419. Now, as G-25 was first put on the market did it [142] contain some monomers and dimers along with polymers? A. Not to the best of my knowledge.

XQ420. Did you make any efforts to remove the monomers or dimers? A. Oh, yes. That was a very careful processing step to do that.

XQ421. And you felt that you got—tell us what you know about how well you succeeded in getting the monomers and dimers out. A. Well, again I think you are asking the wrong man the question, but I can say that just in a general

sort of way that we used a high-vacuum technique and a very critical part of the operation is the removal of low molecular weight materials along with excess glycols. We have always considered it a truly polymeric material. That is why we talk about non-migratability and so forth."

. . . . . .

Deposition of E. M. BEAVERS, witness called by defendant, Laboratory Head of Research Department of Rohm & Haas Company:

Direct Examination.

. . . . . .

[160] Q27. What do you say as to the last sentence on page 1 of the letter? Can you verify that of your own knowledge, if you have such knowledge? A. Oh, yes, I would verify that statement.

Q28. And that is the statement that reads:

"In each of these products no significant change has been made since it was first offered for sale."

And that follows a reference to Paraplex G-25 and G-40, among others. A. (Witness nods head.)

. . . . . .

[165] Q54. What was the reason for the development of G-40, since you already had G-25? Or what were the reasons? [166] A. I think we had two primary reasons for developing G-40. One was that it was lower in cost than G-25. The other was that it was less soluble in hydrocarbon solvents. We thought this might be of some value.

. . . . . .

[167] Q61. And there was and always has been a cost differential between G-25 and G-40, is that not correct? A. Yes, sir, that is correct.

Q62. And a substantial one? A. An important one, yes, sir.

. . . . . .

[180] Q97-½. Is G-20 a suitable plasticizer for VYNW and VYNS A. No, sir, not that I know of. We have tested G-20 at the 35-per-cent level with VYNW and it was not compatible on the mill. But this statement says "and its copolymers." And the copolymers I have in mind are Vinylite VAGH, for example, with which G-20 is compatible.

Q98. Or VYHH? A. Or VYHH to some extent.

Q99. So that for the high molecular weight VYNW and VYNS, the G-20, as you say, would not be a suitable plasticizer? A. To the extent that we have tested it, that was our conclusion.

. . . . . .

[182] Q103. You certainly don't recommend G-20, that is, for use with VYNW or VYNS? A. Not that I know of.

. . . . . .

Q104. Have you ever recommended it to your knowledge for use for those two specific PVC acetate copolymers, namely, VYNW and VYNS? A. Not to my knowledge.

. . . . . .

[190] A. The vacuum stage of the process for the preparation of G-25 has as the purpose the removal of free glycol and water which may result from the polyesterification.

. . . . . .

Q114. Is that conducted at a temperature which tends to remove lower molecular weight material? Are the conditions such that it tends to remove lower molecular weight material? A. I am afraid that in order to answer

that I would have to know how low you mean. That is a matter of interpretation, it seems to me.

Q115. Well, suppose we say material of the order of three, four, 500 molecular weight. A. I don't know that it would remove anything that high in molecular weight.

Q116. Is whatever you have said as to G-25 also true of G-40? A. Yes, sir.

Q117. So whatever is true of one would be true of the other? [191] A. Yes, sir.

Q118. In that respect. Do you regard G-25 as a truly polymeric material? A. In the sense that the polymer chemist usually has in mind, yes, indeed; it is a truly polymeric ester.

Q119. And the same is true of G-40, of course? A. Yes, sir.

. . . . . .

[230] RXQ283. Now, the next paragraph here says:

> "As a group, the Paraplex resins are soft, flexible resins widely used as plasticizers for more brittle film-forming materials such as nitrocellulose, ethyl cellulose, polyvinyl chloride and polyvinyl butyral."

Do you agree with that statement? A. I can think of exceptions to that statement, and I think that statement is not absolutely and broadly applicable if you interpret it literally.

RXQ284. Is it a fair general statement? I understand it to be offered as a general statement. A. It is a general statement which has specific exceptions, yes, sir. It is intended to indicate in a general way that Paraplex resins act as plasticizers. If you come down to particular cases, then you would have to make some exceptions. Paraplex G-20, for example, we were not able to incorporate into VYNW at the 35 per cent level and yet VYNW is a polyvinyl chloride and G-20 is a Paraplex.

RXQ285. Yes. But you are not saying that you were not [231] able to incorporate it at any level, are you? A. I cannot say that, no.

RXQ286. Now, there is a limit to how far you can incorporate G-25 and G-40, is there not, in certain types of these synthetics? They aren't compatible in all proportions, are they? A. I don't know of any limit to the compatibility of G-25 with polyvinyl chloride.

. . . . . .

Deposition of ARTHUR L. BLOUNT, witness called by defendant, Assistant Plant Manager of Resonance Products Division, Rohm & Haas Company:

Direct Examination.

. . . . . .

[241] Q14. Have you manufactured on a plant production basis [242] G-25 ever since you began in April of 1944, as you stated? A. Yes.

. . . . . .

[243] Q23. Now, Mr. John F. Bergin sent attorneys for both [244] parties herein a letter of December 29, 1954, here identified as Defendants' Exhibit 13, which I hand you and ask if you can confirm—

. . . . . .

[245] A. Well, again I can only speak for G-25 at the moment. I haven't reviewed my information on G-40, 50 or 53. I know that there is no significant change in the product in the case of G-25, since its manufacture.

. . . . . .

[247] Q29. Do you say that there was no significant change in the product? A. I said I know of no significant

change in the product since we started the manufacture of it.

Q30. Did the data studied indicate that there was no significant change? A. Of course the only way by which I can pass upon the quality of the product is by reference to the specifications which define the material, and within the specifications that we have established for this material, all the production that we sold complied with those specifications. Now, that is what I mean.

Q31. And do you work closely to those specifications? A. We work very closely with them. In all instances we work closely with the specifications.

. . . . . .

[248] Q34. Is it true that at some late stage of the manufacture of both G-25 and G-40 you have stripped the volatile materials by a high temperature and high vacuum distillation?

. . . . . .

A. I will say yes.

. . . . . .

[249] Q35. Can you tell us if such distillation has continued over some period of time? A. It has, a considerable period of time.

. . . . . .

Q37. Are the time, temperature and vacuum factors calculated to strip the volatile materials by such treatment? A. Well, I could avoid that question by saying that I am not the chemist or the man that developed it, as far as I am concerned. I would have to express an opinion and you don't want opinions.

Q38. Well give that opinion. A. My opinion is yes, that the time and the temperature at which we strip these are sufficient to strip off any volatile material other than the product we are trying to manufacture.

[259] Q39. And you meant to include the vacuum factor, too? A. Yes I did.

. . . . . .

Deposition of JOHN MYERS, witness called by defendant, Manager of Sales Development Department, Resonance Products Division, Rohm & Haas Company:

Direct Examination.

. . . . . .

[259] Q32. Was there some one principal use very early in the history of Paraplex AR-148 and G-25? A. Yes, sir.

Q33. What was that? Tell us briefly. A. As a plasticizer for vinyl used in a cable jacket on high frequency cables.

. . . . . .

Q36. Did you people approach them in the first instance? A. Did we approach the Navy?

Q37. Yes, sir. A. No, they approached us.

Q38. Seeking what? [260] A. Seeking a plasticizer which would do this particular job.

Q39. What was the particular job? A. To give a non-migrating plasticizer for polyvinyl chloride that wouldn't migrate into polyethylene when used as a cable jacket.

. . . . . .

Q44. As a matter of fact, that job gave the product considerable impetus, did it not,— A. Yes, sir.

Q45. —in non-migratory applications? A. It gave it a considerable impetus as a plasticizer for vinyl, at least.

Q46. And you used all of the sales promotion energies you could command to sell the product as a non-migratory— A. We hope the management felt that way.

. . . . . .

[278] Q130. Have you any knowledge as to the curve of sales, so to speak, for G-25 in 1944? A. Not the specific figures. I remember that as a result of this coaxial cable development it developed much faster than we had ever anticipated. What the level was, actually, I don't remember.

Q131. That really gave you the big leg up in the business? A. Yes, sir.

. . . . . .

[314] Mr. Kirkpatrick: Mr. Bergin, you wish to say something concerning Mr. Blount?

Mr. Bergin: I have talked to Mr. Blount by telephone this morning and he tells me there has been no significant change in the composition of Paraplex G-40 since the time it was first manufactured in the plant.

Mr. Kinney: Based on our discussion of yesterday, Mr. Kirkpatrick, we are willing to agree, to [315] save Mr. Blount coming back, that if he were called as a witness he would so testify.

. . . . . .

Excerpts from Deposition of Irving C. Eaton, Taken by Defendant at Bridgeport, Connecticut, April 7, 1955.

Deposition of Irving C. Eaton, witness for defendant, employee of General Electric since 1925, at Bridgeport plant since 1930, and now Consultant, Construction Materials Laboratory:

Direct Examination.

. . . . . .

[3] Q. Did General Electric, to your knowledge, ever manufacture at Bridgeport so-called coaxial electric cable?

A. Yes, we most certainly did, beginning in the early part of World War II.

Q. For what was that used? A. Well, it was used principally for high frequency cable, radar and similar applications.

Q. Was any improvement made in the early part of World War II, particularly a change in insulation? A. Yes. Very fortunately, [4] there was a development by the British, developing polyethylene, which was found to be a very much better insulating media than materials which were used prior to that time.

Q. Will you tell us, generally, the structure or make-up of the coaxial cable? A. Well, in simplest form, you had a conductor, over which was polyethylene insulation, and over that a metallic braid, and over that a protecting thermoplastic sheath material.

Q. What was the material of that plastic sheath? A. Well, it is a polyvinyl chloride composition, plasticized polyvinyl chloride.

. . . . . .

Q. Did you have trouble with this polyethylene when you used it? A. We did have in the early days, principally for the reason that this protective sheath that I have talked about was of such a composition and character that there were migratory conditions, where the plasticizer in the sheath migrated into the polyethylene and "poisoned", as we call it, the polyethylene.

. . . . . .

[5] Q. (By Mr. LeGates) And did you not know that this deterioration which you found by test was due to movement of material from the jacket into the polyethylene? A. Well, we had a composite. We had a construction which involved the use of material which was known to be very good electrically, very low electrical losses, and it was

known that if there would be any great migration, then the electrical characteristics of that underlying insulation would be affected.

. . . . . .

[7] Q. Your work at G.E. at that time required you to know and have familiarity with insulating materials, is that correct? A. That's right.

Q. And with synthetic resinous insulating materials? A. Yes, that is what we were dealing with in this case.

Q. And with plasticizers, used as such? A. Yes. This sheath material which we were using was a type of material which involved the use of a resin—in this case it was polyvinyl chloride—and a plasticizing material, or a plasticizer.

Q. Was the problem of deterioration a matter of concern to the armed forces? A. It was of very great concern to them, for the reason that types of protective sheath material involving the use of migratory types of plasticizers would not do the job.

[8] Q. What did they do to attack this problem? A. Well, the job was tackled pretty much on a nationwide basis. The problem was so important that this thing was tackled pretty much on an industry-wide basis, and the best brains in the business were gotten together to try to solve it.

Q. They were gotten together at meetings? A. Yes.

. . . . . .

Q. What was the solution? A. The solution was the development of a plasticizer which was much less migratory than others which [9] had been used before that time.

Q. What was that? A. This was a material by The Resinous Products Company, which the company called G-25.

Q. Also known as Paraplex G-25? A. Yes, Paraplex.

. . . . . .

Q. When did this occur? A. Well, starting in around 1942, if I remember correctly, and for the balance of the war period.

Q. Was this Paraplex G-25 you have mentioned actually used in the radar cable? A. Yes.

Q. When was that? A. Well, G-25 is still used.

Q. Let me ask you a further question: Was it used promptly after it was brought to light? A. You bet it was, because we had a problem, and G-25 seemed to be the solution to the problem. Therefore, we and others in the business of making high frequency cables went right into the use of G-25.

. . . . . .

Cross-Examination.

. . . . . .

[21] XQ. Well, the losses in electrical energy at high frequencies, measured in decibels, would be some measure of the attenuation value of the insulation? Do I state it correctly, or am I all mixed up on that? A. I think perhaps I would only care to go as far as to say that we were dealing with material wherein electrical losses, of necessity, are to be kept down to a minimum. And the older type of plasticizing material for polyvinyl chloride involved electrical [22] poisoning, as we have termed it. In other words, the plasticizer was of such a nature that it migrated into the insulating material and poisoned it, so-called, and made for higher electrical losses in that insulation.

Therefore, when we were able to get a plasticizer which was less migratory than the older types, there was a very definite gain made. In other words, there was a real contribution made by the Resinous Products people, to the end that you had a better, a more certain insulating material for operation at high frequencies.

. . . . . .

Excerpts from Deposition of Paul Shalita, Taken by Plaintiff in New York, April 20, 1955.

Deposition of PAUL SHALITA, witness for plaintiff, Technical Director and Vice-President of Technical Tape Corporation:

Direct Examination.

. . . . . .

[5-6] Q. Do you know when your company first made and sold a pressure-sensitive vinyl plastic electrical tape? A. It was made first in late 1949 or the first month or so of 1950, and sold approximately in that same period.

. . . . . .

[91] Q. I believe you testified there was some difficulty experienced in making tape with these films; you ran into some difficulties, is that correct? A. I think I testified that on the VUWB 59402, that there was some difficulty until we got the proper adhesive formulation for it.

. . . . . .

[92] Q. Has it been your experience, Mr. Shalita, in making a vinyl plastic electrical insulating tape with a vinyl film backing and some kind of a plasticizer, that one may satisfactorily use any kind of pressure-sensitive adhesive on it? A. No. It's been my general feeling that a specific adhesive had to be formulated for a given film.

Q. Does that depend on the composition of the film in terms of the nature of the resin and the type and amount of plasticizers and type and characteristics of the pressure-sensitive adhesive? A. Yes. I think they all play a part in producing a functionable pressure-sensitive tape.

. . . . . .

[93] Q. Now, in the commercial manufacture of "Tuck" brand vinyl electric tape, has Technical Tape Corporation used any of the specific adhesive formulations disclosed in the Oace patent? A. I think I have already testified it has not.

Defendants' Exhibit 60A.

Swiss Patent No. 206,871
Class 125b

Published December 1, 1939

Application Received February 6, 1939--6:15 P.M.
Patent Entered August 31, 1939
(Priority: Germany, January 5, 1939)

Wilhelm Bierbrauer, Zürich (Switzerland)

Adhesive Tape for the Respective Sealing and Unmasking of Protuberant, Angular or Otherwise Uneven Surfaces

Adhesive films with self-adhering adhesive are well-known with a base of woven material (cotton, wool, rayon, etc.) or from creped paper for applications for technical purposes. Used for example for the closure of boxes (cans), they have the disadvantage that they do not stop air and moisture, a property which is caused by the porosity of such materials.

Films from synthetic material also coated with adhesives are also known: for example cellophane or waxed and coated papers. These films, however, are neither stretchable nor elastic. To be sure, on flat surfaces, they shut out air and water but where protuberances or corners have to be adhered, they are not effective. Thus, they can not be effectively attached on account of their insufficient stretchability and elasticity to articles which have protuberances, hollows, or angles, as for example rectangular boxes (cans).

Thus, these adhesive films are not effective barriers in all cases where it is necessary to shut out air and water.

Finally, there are adhesive films from chlorinated rubber and rubber and wax mixes. These films are air and water tight and to some extent stretch, but they have only slight elasticity and show the additional disadvantage that

they can easily be overstretched, that is by overpulling, they lose continuity in particular spots. Adhesive tapes under this invention obviate these disadvantages by being made from air and water tight deformable, permanently elastic, synthetic films which are coated with a self-adhering, latex-resin mixture.

The above invention rests on the realization that there are certain plastic materials which fulfill all these requirements for air and water tightness, deformability, and elasticity. By deformability, we here understand the property that a material has, when stretched to twice its original length, of losing none of its mechanical strength, that is resistance against tearing, from the unstretched material; and by elasticity, it is understood that the property is not lost, of returning spontaneously to its original dimension upon release of the stretching force. These properties appear in the mixed polymers, for example the vinyl resins which appear in the trade under the trade-name "Mipolam" or in acrylic acid esters which appear in the trade under the name "Flexigum". These films can be treated with self-adhering materials from unvulcanized or slightly vulcanized latex with which resin is mixed and retain their self-adhering properties practically undiminished without any influence on the base material by the adhesive.

The new adhesive tapes unite the deformability and elasticity of adhesive films on woven base with the air and water impermeability of films on a stiff synthetic base, in that they are very tear resistant and as a practical matter cannot be overstretched.

On account of these new unexpected, favorable properties, the new adhesive tapes are not only indicated for closing bottles, boxes (cans), ointment cans, and similar containers which have rounded or angled edges, but also they are very useful for other technical purposes where it is desirable to protect irregular or angular edges during

lacquering operations, as for example in airplane or automobile manufacture.

For these purposes, one can lay down such adhesive films in slightly stretched condition whereby on account of their elasticity, they hold tightly and surround the adhered object with a completely strong water impermeable and air impermeable layer.

Patent Claim:

Adhesive tape for the covering of curves, angles, or other uneven surfaces comprised of an air and water impermeable, extensible elastic plastic film which is covered with a self-adhering, latex-resin adhesive.

Sub Claims:

1. Adhesive tape according to the above claim in which the plastic is a mixed polymer.
2. Synthetic tape according to the above claim in which the synthetic polymer is a mixed polymer of vinyl resin.
3. Adhesive tape according to the claim in which the plastic is an acrylic ester polymer.

Excerpts from Discovery Deposition of R. W. Lundbohm, Taken by Defendant at Boston, Massachusetts, June 9, 1955.

Deposition of R. W. Lundbohm, witness called by defendant, employee of Minnesota Mining & Manufacturing Company for ten years as a chemist in the Tape Laboratory:

Direct Examination.

. . . . . .

[4] Q9. And I assume from that that it is the custom for Minnesota, and has been during your time, to analyze competitors' tapes periodically? A. Yes, sir.

. . . . . .

Q11. And those competitors' tapes that you have analyzed include plastic electric tape presumably made by Plymouth Rubber Company, is that not so? A. Yes, sir.

. . . . . .

[14] Q66. I will pass by the next document, which seems to be of [15] no significance. Now we next come, Mr. Lundbohm, to "Analytical Test Report-Tape Department-AR-1086," dated May 28, 1951, and bearing at the end your name, R. W. Lundbohm, is that not correct? A. Yes, sir.

Q67. The subject of this test report was "Competitive Plastic Electric Tapes," is that not so? A. Yes, sir.

Q68. Then you have a paragraph entitled "Background." It states, "Quantitative and qualitative analysis of the plasticizers being used by competitors in the plastic electric tape field has been requested relative to the claims which the Patent Office has allowed 3M." 3M is your designation for Minnesota, I take it? A. Yes, sir.

. . . . . .

Q70. Now the next paragraph is entitled "Analyses." It states in substance that extractions from the backing, free from adhesive, were performed in Soxhlet extractors and that the composition of each extract was ascertained by comparative infrared absorption spectra run by Central Analytical Research. Now by samples you mean samples of the plasticizer, is that not so? A. Yes, sir.

. . . . . .

[16] Q72. From which they can determine the character of the plasticizer, is that so? A. Yes, sir.

. . . . . .

[18] Q81. Now at the bottom are three samples entitled "3M Co.—Control Samples." Those, I take it, are samples of Minnesota commercial plastic electric tapes analyzed

for comparative purposes, is that correct? A. The three with the number 33 are Minnesota tapes, yes, sir.

Q82. Now the first tape of the ten competitors' tapes states that the type of plasticizer was "polyester and phosphate." Now phosphate indicates that there was some monomeric plasticizer together with the polyester? A. That is correct.

Q83. And all the other nine show that the plasticizer was polyester, is that correct? A. Yes, sir.

. . . . . .

Q85. Now the three control samples all have a plasticizer comprising a combination of polyester and phthalate, is that not so? A. Yes, sir.

. . . . . .

[20] Q93. Now, Mr. Lundbohm, Mr. Kinney sent us also some copies—

Mr. HOLMES. I take it these are copies, Mr. Kinney, and not originals?

Mr. KINNEY. Yes. It is my understanding that they are copies.

Q94. —of what might be termed infrared tracings, among others, the one which I have in my hand and which I will show you in a little while. In the upper right-hand corner is a stamp "Central Research Laboratory—Test No. 6980, Date 5/10/51. Sample Plasticizer, Plymouth elect. tape. Origin Lundbohm." Is that not correct? A. Everything that you read is correct.

. . . . . .

Q97. Was it on the basis of this tracing, this infrared tracing that you recorded in the test report, Defendants' Exhibit 58-F, [21] Report No. AR-1086, that the plasticizer of the Plymouth Rubber Company sample, TSC-2754, was "polyester"? A. Yes, sir. It was on the basis of infor-

mation furnished us by the Central Analytical Research Laboratory that we made this entry on AR-1086.

Mr. HOLMES. I will have this infrared tracing marked Defendants' Exhibit 58-G for identification.

[Infrared tracing marked "Defendants' Exhibit 58-G for identification."]

Q98. Written in longhand on the body of the tracing are the words "All Paraplex G-40," as you will note? A. I see that notation, yes, sir.

. . . . . .

[22] Q103. There are records earlier than May of 1951 of tests of competitors' tapes which are not included in this file? A. I don't know that.

Q104. Have you made any effort to ascertain that? A. I haven't made that effort.

. . . . . .

[32] Q140. Now, Mr. Lundbohm, at the bottom of the page of Defendants' Exhibit 58-F for identification, page 1, and at the top of page 2, there is a substantial obliteration. Now did the matter which is here obliterated have reference to patent claims in any way? A. I can answer that very easily. I don't have any idea what was obliterated. I would have to go back to the original sheet to see that.

. . . . . .

Q143. Would it be your custom in submitting a test report of this character to make any comment as to what is recorded? A. It would not be our custom to comment on it.

Q144. I note in your report of November 9, 1950, being Exhibit 58-C, following the description of the adhesive backing and the primer, there is a paragraph entitled

"Discussion." Now in that report you did follow the description of what you found by some comments, is that not so? A. Yes, sir.

. . . . . .

[35] Mr. HOLMES. Now, Mr. Kinney, I asked you to bring with you the original of the analytical test report, Defendants' Exhibit 58-F of May 28, 1951, and indeed all obliterated documents, so that if it appear that we are entitled to see the obliterations, what is obliterated, or at least for the purpose of determining whether it was material properly obliterated. Now have you done so?

Mr. KINNEY. No, sir.

Mr. HOLMES. Do you know what was obliterated?

Mr. KINNEY. I don't know now. I could certainly very easily find out.

. . . . . .

[37] . . . Now you made claim—I have specific reference to the obliterations at the bottom of page 1 and the top of page 2 on Defendants' Exhibit 58-F—that the material obliterated was of a "confidential nature." Might I ask if that material had reference to or was concerned with any trade secret of Minnesota of any character, business character or technical character? May I ask that question?

Mr. KINNEY. You certainly may ask the question, Mr. Holmes, but I'm in no position to give you an answer.

. . . . . .

[39] Q155. Mr. Lundbohm, so that you may refresh your recollection or determine the nature of the obliterated material on Defendants' Exhibit 58-F for identification—and I would not be asking you at this time necessarily to state exactly [40] what the language is—will you take Mr. Kinney's copy which has tape on the obliterations and see if you can't peel that off to disclose the material underneath

so that you can then tell me the general nature of the obliterated material? A. I don't know if I would be permitted to do that.

. . . . . .

Mr. KINNEY. I certainly decline to give him these work papers.

. . . . . .

[*Proceedings before Judge Ford.*]

. . . . . .

[59] The WITNESS. I have no memory of what is beneath that tape. It will be as revealing to me as anyone. I have no memory of what is beneath there.

The COURT. I'm not too sure I believe you.

. . . . . .

[65] The COURT. Let me determine that. Is it your point that it is of a confidential nature?

Mr. KINNEY. Yes.

The COURT. That is a different point. Now if counsel will retire, I want to expedite this matter [66] as reasonably as possible, and my own law clerk will remain.

[At this point Mr. Holmes, Mr. Kirkpatrick, Mr. Lundbohm, Mr. Sheehan retired from the room for a period of fifteen minutes.]

The COURT. I have talked to Mr. Kinney about this matter and as a result of our discussion he has agreed to exhibit to you what is under the tape.

. . . . . .

The COURT. I don't know what it amounts to at all, but it doesn't seem to me to be involving a secret process.

. . . . . .

Excerpts from Discovery Depositions of Esther E. LeI'age, Warren D. Hurd, Ralph J. Oace and William E. Lundquist, Taken by Defendant at St. Paul, Minnesota, January 31–February 4, 1955.

Deposition of ESTHER E. LEPAGE, formerly Esther Eastwold, one of the patentees of the Oace *et al.* patent in suit, and an employee of Plaintiff, as a chemist, from about June, 1943, to April, 1951:

Direct Examination.

. . . . . .

[11] Q. Is it also correct that Dr. Lundquist was a member of that group at that time when you went to work? A. At the time when I went to work, Dr. Lundquist was part of that group under Dr. Hendricks.

. . . . . .

[20] Q. What sort of plasticizers did you use at the outset of your work with the vinyl polymers? A. We used monomeric plasticizers and polymeric plasticizers, or high viscosity plasticizers and low viscosity plasticizers.

Q. Will you please name the plasticizers you used at the outset? [21] A. I couldn't remember that. In a program of this kind, you consider many materials, and we considered the monomeric plasticizers. We used dioctyl phthalate—

. . . . . .

Q. (By Mr. Kirkpatrick) You have named dioctyl phthalate as one of the plasticizers. Can you name any of the other plasticizers of that caliber that you employed? A. Well, as I recall, there were many. We tried—tricresyl phosphate was one. I'm sure that there are trade names which I cannot remember now.

Q. Would you refer to each of those as a low molecular weight and monomeric plasticizer? A. Yes, I would.

. . . . . .

[22] Q. Now, you referred to high molecular weight plasticizers. Which of those did you employ first? A. I cannot remember which one we used first.

Q. Can you name any of those? A. We did use a "Paraplex G-25".

. . . . . .

Q. Is it correct to say that you cannot now name any other high molecular weight plasticizer than the G-25 that you used at that time? I am talking about that time, meaning about a year after you came there as you stated. A. I cannot remember exactly when all this—we evaluated other polymer plasticizers. I cannot remember when that work [23] was started.

Q. Or what they were? A. Well, we arrived at a combination in this Paraplex G-25 and DOP that satisfied our requirements very nicely, and it was the best—we were concerned in making a good product.

Q. Can you recall the names of any other high molecular weight viscous resinous plasticizers that you employed other than G-25? A. I think there are other ones listed in the patent.

Q. But you cannot now recall their names? A. Well, I think that polyethyl acrylate is listed, is it not?

. . . . . .

[33] Q. When the use of G-25 was first suggested to you, was it suggested as a non-migratory resinous plasticizer? A. I think that's what it was claimed to be.

. . . . . .

[38] Q. Did you ever employ bodily pressure-sensitive adhesive coatings from other departments or divisions of

people at 3-M? A. I got the adhesive from other departments.

. . . . . .

[42] Q. Is it correct to say that you have no recollection of Dr. Lundquist telling you that if you used monomeric plasticizers only, the adhesive applied to the backings would go pasty? A. That was well known throughout the company and I'm sure throughout the industry.

. . . . . .

[137] Q. All right. Now, when it came to the matter of the question of a reissue,—who first raised that question with you? A. I can't exactly remember who it was that first raised it.

. . . . . .

Q. And how long was that after the issue of your original patent?

. . . . . .

[138] A. It was within the year following that.

Q. (By Mr. Kirkpatrick) Can you place it any more accurately than that? A. It was in the summertime, before that reissue application was filed.

Q. Do you mean the summer of '51 or summer of '52? A. The summer of '52.

. . . . . .

[139] Q. Can you recall more than one meeting? A. No.

Q. Where was such meeting held? A. In St. Paul.

Q. Where in St. Paul? A. In the hospital.

Q. You were in the hospital at that time? A. Yes.

. . . . . .

[152] "Question: Can an adhesive pressure-sensitive insulated tape with vinyl polymer film backing, having the properties described in your patent, be made with

satisfactory results using only a viscous, non-migrating plasticizer resin, or resins?"

A. You are asking me a question now of work that I have been away from for a long time. I am not sure what can be made now.

. . . . . .

Q. (By Mr. Kirkpatrick) Do you know the answer to the question?

. . . . . .

[153] A. I have to say I don't know.

. . . . . .

[155] "Question: Do you state anywhere in your patent that the use of a plasticizer (or plasticizers) in addition to resinous plasticizers is optional or permissive?"

A. I think that in claim No. 6 of the patent that it is optional whether you add the non-viscous plasticizer.

. . . . . .

Deposition of WARREN D. HUBB, employee of plaintiff, connected with Tape Laboratory from 1937 to early part of 1944:

Direct Examination.

. . . . . .

[186] Q. In an affidavit in this matter you have referred to certain work you did in connection with the making of stretchable pressure-sensitive tapes. Will you please state what that work was, what you did, the results, and so forth? A. Well, I did quite a bit of work and I can't remember it all just off-hand, without looking at the records, but it was

in the direction of developing a stretchable plastic tape to be used for binding the insoles of women's shoes, and the results were all poor.

. . . . . .

[189] Q. Now, you indicated that you had poor results. I have forgotten your exact language. What did you mean in that regard? A. Well, all my adhesives went pasty. They all softened up.

. . . . . .

Q. At any rate, migration was the accepted reason for the behavior of the adhesive in going pasty? [190] A. Yes.

. . . . . .

Deposition of RALPH J. OACE, one of the patentees of *Oabe et al.* patent in suit, an employee of plaintiff since January, 1937:

Direct Examination.

. . . . . .

[214] Q. (By Mr. Holmes) That's just reasoning, Mr. Oace. Did you know, or when did you know, or did you always know that there was some viscous, non-migrating, resinous plasticizer which when used alone could be successfully so used without loss of tack? A. I don't know when I actually heard, or how I heard. . . .

. . . . . .

[215] Q. (By Mr. Holmes) Well, did you learn or hear that before or after January, 1946 when you filed the original application? A. I really don't recall. I can't place it in that time —

. . . . . .

Deposition of WILLIAM E. LUNDQUIST, chemist in employ of plaintiff since spring of 1942:

Direct Examination.

. . . . . .

[220] Q. . . . You know, of course, that Esther Eastwold LePage has testified in this matter. Was she under you from the inception of her work with the 3-M Company? A. As I recall it, yes, sir.

. . . . . .

[226] Q. While you were with DuPont, did you have any experience in connection with patent applications, patents, and so forth? A. Yes.

Q. And continued to have, of course, with 3-M? A. Yes.

. . . . . .

[229] Q. (By Mr. Kirkpatrick) Have you any recollection or can you say when you first learned of Paraplex G-25? [230] A. Somewhere around the start of 1944.

. . . . . .

[233] Q. Is it correct to say that G-25 is a soft viscous, low acid number, alkyd plasticizer resin? A. Yes.

Q. Is the same true of G-40? A. Yes.

Q. And each is of high molecular weight? [234] A. For a plasticizer they are pretty high.

. . . . . .

[237] Q. Was this test of G-50 or G-53, whenever it was made, the first time you had obtained such results with a single resinous modifier or resinous plasticizer?

. . . . . .

Q. (By Mr. Kirkpatrick) Either made or supervised, Doctor. I don't necessarily mean that you did it with your own hands. A. I can't remember. I would guess no, but that's a guess. It's not reliable.

Q. Had you ever heard of that result being obtained by anybody else before you made such test? A. No.

. . . . . .

[240] Q. (By Mr. Kirkpatrick) The reissue patent refers to a "cucohesive normally tacky and pressure-sensitive rubber-resin type" of adhesive. Was that a standard adhesive with the 3-M in 1944? A. Yes. Before I be so rash, — the terminology was standard. Just exactly which adhesive — where are you referring?

MR. HOLMES: Well, in Claim 1.

A. (Continuing) Oh. The terminology is standard if it's in Claim 1, — yes.

Q. (By Mr. Kirkpatrick) And similarly, was a water insoluble normally tacky and pressure-sensitive rubber-resin type of adhesive a standard adhesive with the company in 1944? — that language coming from Claim 6. A. Under the subheading (3) there, you mean? — yes.

. . . . . .

[252] Q. Now, how about G-40? Was there any change in that as originally received? A. I am not aware of any change.

. . . . . .

[254] Q. Are some adhesive compositions more subject to migration than others? A. Oh, yes.

Q. Are some adhesive compositions more subject to loss of tack than others?

MR. KINNEY: In what connection, Mr. Kirkpatrick?

MR. KIRKPATRICK: In their use on vinyl-polymer backed tapes of the invention. And I meant, of course, the same in the preceding question.

MR. KINNEY: I just thought it might make the record a little more definite.

MR. KIRKPATRICK: Right.
A. Yes.

. . . . . .

Excerpts from Testimony at Trial.

HUBERT JAMES TIERNEY, witness on behalf of plaintiff. Vice-President of plaintiff in charge of all tape research and tape manufacture of plaintiff:

Direct Examination.

. . . . . .

[47] A. I can recall specifically that in 1938 I made a number of attempts to make a satisfactory vinyl film-back pressure-sensitive adhesive tape. . . . All attempts were unsatisfactory. The pressure-sensitive adhesives became very soft and gooey and pasty and in any attempt to unwind the rolls the adhesive split, leaving half of the adhesive on the back side of the underlying layer of backing.

Q. Did you form any opinion as to why it was difficult to make a commercially successful pressure-sensitive tape at that time; I mean the reason for your failure? A. Yes. . . . [48] The pressure-sensitive adhesives absorbed the migratable, oily type plasticizers that were then used to plasticize the polyvinyl chloride, or vinyl chloride-vinyl acetate copolymer resin, and in the process of being added to the pressure-sensitive adhesive they spoiled the original character of the pressure-sensitive adhesive.

. . . . . .

[52] A. Yes, they obtained a successful conclusion and solution to that project or problem in October of 1944.

Q. Will you tell us briefly how that first tape of this type was made? A. The tape was made with a pliable and stretchable plasticized polyvinyl chloride-vinyl acetate film backing; in other words, they utilized a vinyl chloride-vinyl acetate copolymer resin, namely, VYNS. That resin was plasticized with a non-volatile, non-migrating plasticizer comprising Paraplex G-25 and dioctyl Phthalate. The film backing was primed and coated with a pressure-sensitive adhesive.

[53] Q. I understand this tape was later made commercially; is that correct? A. Yes, it was. It was sold in 1945 and formulations substantially the same as that have been sold continuously up to the present time.

. . . . . .

[87] A. . . . The plasticizer, the liquid type plasticizer has migrated from the backing into the adhesive, making it very soft and gooey and valueless.

. . . . . .

[103] Q. Well, can a viscous liquid polymerized ethyl acrylate be divided into a low-molecular-weight fraction and a high-molecular-weight fraction? A. Yes, very definitely you can fractionate the polymerized resin onto a low-molecular-weight liquid fraction and into a higher-molecular-weight liquid fraction, more viscous resinous fraction.

. . . . . .

[121] Q. . . . Now, first, Mr. Tierney, what is a copolymer? I don't believe we have had that defined. A. A copolymer is the combination of two monomeric materials, that is, different monomeric materials.

Q. Then do we understand that they mix together the vinyl choride and the vinyl acetate in certain proportions, that each is in monomer form, and then polymerize the mixture; is that the way it's accomplished? A. Yes, originally

they would take the vinyl chloride monomer in the proportion of 89 parts by weight and combine it with the vinyl acetate monomer in the proportion of 11 parts by weight and copolymerize them to higher molecular weight material, namely, to make a copolymer, [122] or a copolymer of those two materials, in which the vinyl chloride would be present in major proportion.

. . . . . .

[134] A. Yes, Minnesota Mining and Manufacturing Company has sold a considerable quantity of stretchable pressure-sensitive insulating tape that corresponds essentially to example 1, . . .

. . . . . .

[143] Q. Now I think generally we've covered the patent. I have some other questions now. Has the material that is sold by Rhom & Haas, and was sold by them under the trade designation of Paraplex G-25, undergone any observable change over the years, that is, from the time it was first brought to the attention of your company? A. Yes it has. In 1944 to 1945 the Paraplex G-25 that we received, had a film of oil on the surface of the containers, and the Paraplex G-25 which we have received in recent years, has had no such liquid oil on the surface of the containers as we receive it from Rhom & Haas Co.

Q. Now is there any other difference between the recent supply of this Paraplex G-25 as compared with that furnished to your company by Rhom & Haas in the year 1945? A. Yes, the observable difference that today when we utilize the current vintage type of Paraplex G-25, we can make a satisfactory stretchable and retractable pressure-sensitive adhesive tape, with it as the sole plasticizer. We had no success in doing that in the period 1944 and 1945 because such tape as was made with the Paraplex G-25 of [144] that

vintage, lost its pressure-sensitive adhesiveness within one or two days after the tape was made. . . .

. . . . . .

[164] Q. Mr. Tierney you said this morning that Van Cleef reached the market in 1949. What other competitor manufacturer reached the market? A. The next competitive imitation of the Oace patented product reached the market in the last part of 1949 and the early part of 1950. That was the plastic tape manufactured and sold by Technical Tape Corporation.

. . . . . .

[166] Q. Now Mr. Tierney, have you an example of the material known as the polymerized ethyl acrylate? A. Yes I do.

Q. All right, the bottle that is before you, I ask to be identified as Exhibit T-18. Now, what's the nature of this material? A. This is a soft viscous resinous material, somewhat [167] more viscous than the Exhibit 17 that I just talked about. It is a high molecular weight resinous material.

Q. Well, how does its physical characteristics compare with a plasticizer of the material that is contained in Exhibit 17, which was the G-25 plus the DOP? A. It is a liquid material, somewhat more viscous in character than Plaintiff's Exhibit T-17.

. . . . . .

[171] Q. Now have you a sample of the tape that was made with the G-25 of the current production, that is, of the current vintage, as the sole plasticizer? A. Yes, I do.

Q. I believe that is identified as Exhibit T-21 and so marked?

. . . . . .

A. . . . That plasticized film was primed with the primer number 2 of the [172] Oace patent and coated with pressure-sensitive adhesive of Example Number 5 of the Oace patent. The backing is 4 mils.

I might mention at this time that the 3.6 parts of stabilizer was also used in the Example T-19, which utilized G-40 as the sole plasticizer. The .7 parts of carbon black was also utilized in the T-19; and the T-19 also has the primer number 2 of the patent and the pressure-sensitive adhesive of Example No. 5 of the patent.

. . . . . .

[173] A. Yes. The bottle sample that I now have in front of me represents G-25 of current vintage. It is Exhibit T-22.

. . . . . .

Q. Can you indicate the characteristics of it as to viscosity and so forth? A. It is a liquid, viscous resin. As I turn the bottle on its side, you will notice that its viscosity is somewhat higher than the viscosity of the Paraplex G-40, but it is liquid and viscous and it is resinous.

. . . . . .

[176] Q. Have you analyzed this G-25, current G-25, to determine the range of molecular weights? A. Yes, I have had such current-vintage Paraplex G-25 analyzed for its percentage composition of the different molecular-weight fractions.

Q. Do you remember the range? A. Yes. The molecular weight ranges from one thousand to approximately fifty thousand.

. . . . . .

[177] A. Yes, T-20 is the Paraplex G-40 itself, as it is sold by the Rohm & Haas Company. Exhibits T-24 and T-24-A represent the fractional parts of the original Paraplex G-40 that is represented by Exhibit T-20. In other words,

in this bottle, namely, Exhibit T-24, we have 67 per cent, which is the more viscous, higher-molecular-weight resinous portion of the Paraplex G-40, or the Paraplex G-40 as represented by Exhibit T-20. Exhibit T-24-A represents 33 per cent of the original Paraplex G-40, which is the more liquid, lower-molecular-weight part of the original Paraplex G-40. If I add these two bottles [178] together and homogeneously mix them, that is, the Exhibit T-24 and the Exhibit T-24-A, I get six ounces, exactly the same thing that I have in Exhibit T-20; I get the original Paraplex G-40 back again.

. . . . . .

[179] Q. (By Mr. Kingsland) Now is the liquid fraction, that is, the material exemplified by the material contained in the bottle marked 24-A, a plasticizer A. It is.

Q. Is it an ester plasticizer? A. Yes, it is.

Q. And is it a liquid ester plasticizer? A. Yes, it is.

Q. Is it a liquid phthalyl plasticizer? A. No.

Q. Well, what is it? A. It's a liquid adipyl plasticizer.

Q. What is the relationship between a liquid phthalyl ester plasticizer and an adipyl ester plasticizer? A. They are both plasticizers; they are both esters of organic dicarboxylic acids; they are both liquid; they are both nonvolatile.

. . . . . .

[180] Q. Well now, what conclusions do you draw in respect to the similarity or difference in function between this liquid ester fraction of Exhibit 24-A when combined with a high molecular weight fraction from Exhibit T-24 as compared with the function of a liquid phthalyl ester plasticizer when combined with a high molecular weight Paraplex G-25 in current production? A. The conclusion that I draw is that the same function is obtained in both cases, and the same end result is obtained by the same method of blending

and procedure. [181] In the mixing of the low molecular weight, ester plasticizer of Exhibit T-24-A, with the viscous alkyd resin plasticizer of Exhibit T-24, a plasticizer is obtained that gives essentially the same function as the combination of the Paraplex G-25 in the ratio of 2 parts to 1 part of DOP. Now, that same result is obtained by using the two parts of the viscous resinous material of Exhibit T-24 with 1 part of the liquid low molecular weight ester of Exhibit T-24-A.

. . . . . .

A. Yes, I have had Paraplex G-25 of current vintage fractionated in the same manner as utilized in the fractionation of Paraplex G-40, and the two bottles that are now in front of me, namely, Exhibit T-25 and Exhibit T-25-A, represent the results of that fractionation. You will notice that this time the amount of the low molecular weight liquid fraction is about half that amount that was [182] fractionated from the Paraplex G-40. In this case, with the Paraplex G-25, the liquid fraction of low molecular weight that was separated from the original Paraplex G-25, amounted to approximately 12% of the original Paraplex G-25. That 12% portion of liquid material is represented by Exhibit T-25-A, and as I turn the bottle on its side you can see its liquid character. The Exhibit T-25 represents the viscous higher molecular weight resin portion, namely, 88% of the original Paraplex G-25.

. . . . . .

[183] Q. Now, there has been a discussion about these phthalyl esters, the sebacic acid esters and the adipic acid esters. What generally is the relationship between these esters? A. They are all liquid plasticizers offered in commerce, in the same grouping and referred to in the literature in the same groupings. They are each the ester of a di-carboxylic acid, namely, the phthalyl ester is the ester of

the di-carboxylic phthalic acid, the sebacyl ester is the ester of the di-carboxylic sebacic acid and the adipyl ester is the ester of the di-carboxylic adipic acid.

. . . . . .

Cross Examination

. . . . . .

[230] XQ. Now I think, Mr. Tierney, you said that Minnesota made some 300 different kinds, as I remember it, of pressure-sensitive adhesive tapes. Is that correct? A. Yes sir. At the present time we have over 300 different standard tapes of pressure-sensitive adhesive tapes that are being marketed.

XQ. In 1940, let us say, I presume you didn't have as many as 300 but you had a great many at that time? A. We had a great deal less than 300 in 1940. I believe, however, that even at that time we were probably marketing at least 90 or 100 different types of standard pressure-sensitive adhesive tapes.

. . . . . .

[231] XQ. Now each of these materials, I assume, were selected because of its properties in relation to the end use, so to speak? A. Yes, it had a great deal to do with that in many instances.

XQ. Now, all these tapes that I have just been speaking about back in 1940, all had pressure-sensitive adhesives, and those pressure-sensitive adhesives, I assume, were cuco-hesive as defined in the patent, that is, more cohesive—had more cohesive strength than adhesive strength. Is that not correct? A. Yes.

. . . . . .

[237] XQ. Now you've testified that the rubber electricians' tape has a dielectric strength of about 350 volts per

mil and that the Scotch tape No. 33, your electric tape vinyl backed, has a dielectric strength of 1200 to 15,000 volts per mil. 1200 to 1500 volts? A. Yes sir.

XQ. That is because the vinyl chloride material has that inherent property of high dielectric strength as distinguished from the property of the rubber, which is less effective. Is that not so? A. The polymerized vinyl chloride resin itself, when sheeted in sheet form, has a higher dielectric strength than the uncured rubber.

XQ. And it was known— A. Of equivalent thickness.

XQ. And it was known prior to 1940 that polymerized vinyl chloride sheets of this character did have this excellent quality? A. Yes.

XQ. And for that reason had been used for insulation? A. Yes, they had been used as extruded compounds around copper conductors.

XQ. Well, they did make tapes of this material for electrical [238] uses as I understand. Those tapes had that same dielectric strength I assume? A. Yes, tapes made of the straight vinyl film alone, without any adhesive, and as I testified, were used for insulation purposes, and regarded generally as superior to the rubber tapes, that is, the rubber electrician tapes.

. . . . . .

[247] Is there any significance in the reference, in the first place, in line 41, column 1, to a liquid type plasticizer, and then over at column 5, in the first paragraph, it says many liquid plasticizers; is there any difference between liquid and liquid type that you know of?

The Witness: In that particular two places only, where Mr. Holmes has had me draw reference to in the patent, there is no difference, because dioctyl phthalate, which appears as the liquid type plasticizer in column 2, line 41, and the specific liquid plasticizers that are mentioned in

column 5, lines 1 to 16, could similarly be called liquid type plasticizers, that is, tricresyl phosphate, dibutyl phthalate, butyl phthalyl butyl glycollate is liquid type like dioctyl phthalate, or DOP, and if these plasticizers are used in more than twenty parts per hundred parts of the vinyl resin they will produce pastiness, as the patent states.

. . . . . .

[252] A. The patent states, at line 34, column 3, that Paraplex G-25 is a preferred example of a suitable resinous type plasticizer which is of high-molecular-weight material, namely, one of a number of high-molecular-weight [253] plasticizers that the patent specifically mentions.

XQ. All of which can be properly catalogued as of the resinous type? A. Yes, they are all resins; they are different kinds of resins. Polymerized ethyl acrylate is a different type of high-molecular-weight resin than the Paraplex G-25. Both of them are high-molecular-weight plasticizing modifiers for the vinyl polymer film. Polymerized vinyl butyl ether is a still different type mentioned in the patent.

. . . . . .

[254] XQ. That isn't my question. This paragraph twice refers to "resinous type plasticizers" and they mention three, Paraplex G-25 and in the same paragraph polymerized ethyl acrylate and as another example, polymerized vinyl butyl ether. Now, those are all three a resinous type of plasticizer are they not? A. They are all resinous type plasticizers . . .

. . . . . .

[256] XQ. Would it be equally accurate to say that that backing comprised a—the plasticizer comprised a mixture of G-25 and DOP instead of saying it is a blend. Mixture would be more accurate would it not? A. The plasticizer

comprised a mixture of 2 parts of Paraplex G-25 to one part of Djoctyl Phthalate.

XQ. Now, each of those constituents maintains its identity, so to speak, in the mix, does it not: For instance, you can subject it to a vacuum and the DOP will come off. There has been no chemical union of the two, so to speak? A. There has been no chemical union between the Dioctyl Phthalate and the Paraplex G-25. It is a physical combination of the two materials.

. . . . . .

[259] XQ. Well, paragraph 3—column 3, line 34, says that Paraplex G-25 is a preferred example of a suitable resinous type plasticizer, and it says that another of these materials is polymerized ethyl acrylate, then another example, G-25 being the preferred, is polymerized vinyl butyl ether. Those are all three resinous types of plasticizers I gather, of high molecular weight. Is that not so? A. Yes they are.

. . . . . .

[263] Now the patent points out there that, to get the permanent equilibrium and also the stretchiness, you should utilize a combination of modifiers, one of which is a liquid plasticizer of low molecular weight, combined with a high molecular weight resinous type plasticizer. Now that language does not exclude the case where the material, the plasticizing material itself, can have both the low molecular weight liquid plasticizing material along with the high molecular weight resinous type plasticizing material, because in a separate sentence, starting in column 3, line 40: "Another high-molecular-weight plasticizer material which has been found useful in providing suitably stretchable and elastic vinyl polymer films is polymerized ethyl acrylate and polymerized ethyl acrylate has both low molecular weight liquid plasticizer and high-molecular-weight resinous plasticizer in it, in the same material, [264] in the

the same way that Paraplex G-40 has both the low-molecular weight liquid plasticizer present in it along with the high-molecular-weight resinous plasticizer.

. . . . . .

[276] XQ. Did they try the home made G-25 as referred to in column 5, line 26? Did they try that as the sole plasticizer? A. I have no specific recollection, but may I explain that I am sure that they must have tried that as well as the polyethyl acrylate and the polymerized vinyl butyl ether because I am sure if they had not tried them, the references that are contained in this patent would not be within the specification.

. . . . . .

[277] XQ. Did this home-made Paraplex G-25 have an oil film on it? A. No, sir. . . .

. . . . . .

[288] A. Oh, if I understand your question correctly, you are asking how long we continued the use of the formula comprising 100 parts of the vinyl polymer resin in conjunction with the plasticizer comprising 28.6 parts to 40 parts Paraplex G-25 or Paraplex G-40 and 14.3 parts to 20 parts dioctyl phthalate, based on 100 parts of vinyl resin, along with approximately 3.6 parts of calcium stearate stabilizer, or the equivalent.

XQ. I didn't say anything about G-40 in Example 1. [289] How long did the use of G-25, with the DOP, remain as the sole formula?

The Court: As shown by Example 1—that's what you have been talking about.

XQ. As shown by Example 1.

. . . . . .

[290] A. We started to use Paraplex G-40 in 1946 and 1947.

XQ. Now G-40 you substituted for the Paraplex G-25 in substantially these same proportions of Example 1; is that so? A. Yes.

. . . . . .

[291] A. That has continued up through 1953. . . .

. . . . . .

[292] XQ. When did you first make commercially, tape in which the backing was plasticized with a resin plasticizer as the sole plasticizer? A. I believe 1953 was the first year.

XQ. And since '53, has that continued, the manufacture of the tape with the resin plasticizer that's the sole plasticizer? A. Yes, for a very small percent of our total volume. The major part even today, is essentially the same as the examples of the Oace patent.

. . . . . .

[296] XQ. Now, the liquid type of plasticizer as exemplified [297] by DOP, is a low molecular weight plasticizer. Is that not so, somewhere around 390? A. The molecular weight of DOP is 390. It is low or high, depending upon what it is being compared to.

XQ. Now those molecular weights are specific molecular weights. Every molecule is the same. Is that not so? Substantially the same? A. The molecular weight of each molecule of DOP is the same weight, yes.

XQ. Now that holds true also does it not for the other liquid type plasticizers enumerated in column 5, the first paragraph? A. The specific liquid plasticizers mentioned in column 5 between the lines from 1 to 9, all are similar to DOP in that respect.

XQ. Now DOP and these others are not only of low molecular weight but they are generally classed, are they not, as migrating plasticizers? A. Yes, when used along with vinyl chloride or vinyl copolymer resin films, they are termed migrating plasticizers.

XQ. Now these plasticizers also are very fluid. They will pour almost like water? [298] A. They are more viscous than water. They are quite fluid.

XQ. Very fluid. That's very fluid is it not? (Indicating Exhibit T-23 in the bottle)? A. Yes, they are more viscous than water.

The Court:

Q. It is descriptive, though, of a liquid plasticizer isn't it? A. Yes.

. . . . . .

[300] XQ. Have you ascertained what the weight distribution of G-40 is? A. Yes sir I have.

XQ. The range? A. Yes sir I have.

XQ. How is that range? A. That ranges from 1000 to 50,000, but the molecular weight distribution indicates that there is present in it [301] a far larger quantity of lower molecular weight material than is present in the Paraplex G-25.

. . . . . .

[302] XQ. But it remains resinous does it not? A. Yes, the portions of Paraplex G-25, the molecules and the parts of it, would all probably qualify for the term resin.

. . . . . .

[303] XQ. Now, as to T-24, what you would term the light fraction remains a resin, T-24-A, a non-migrating resin plasticizer, does it not? A. I believe you have two sections in your question, or two parts of it. My answer to the first part is that the low-molecular-weight portion, the liquid part, Exhibit T-24-A, is properly termed a resin. I have forgotten now the second part.

XQ. And it is a non-migrator; is that not so; it would be so classed? A. It is non-migrating when it is combined with its complementary portion, namely, the higher-molec

ular-weight, as that viscous alkyd resin portion of the Paraplex G-40, which is exemplified by Exhibit T-24.

XQ. Is it not substantially non-migrating by itself? A. It is non-migrating under what conditions and with what, sir?

XQ. Well, any vinyl chloride? A. Under what conditions, sir?

[304] XQ. Normal conditions, in a tape. A. In the pressure-sensitive adhesive tapes such as we are talking about here?

XQ. Yes. A. I believe it would be non-migrating. Certainly it would not migrate as much as the dioctyl phthalate.

. . . . . .

[305] A. Those materials were fractionated by George Rathman of our polymer section at my request within the last forty days.

XQ. And these are the results that he handed out to you? A. Yes they are.

XQ. Did you see the fractionating process proceed? A. No.

[306] XQ. Now when did you make the polymerized vinyl ethyl acrylate which you said was fractionated by Dr. Rathman? A. Your question had reference to the tape?

XQ. No, the polymerized ethyl acrylate which is Exhibit T-18? A. That material was produced sometime within the last 40 or 50 days.

. . . . . .

XQ. Now, take T-24-A which is the less viscous fraction of the G-40, which was T-20, what is the molecular weight of that fraction? A. The weight average molecular weight of the material [307] of Exhibit T-24-A is 5300, so that the approximate number average molecular weight on that basis would also be approximately half, in the range of 2500, indi-

cating that the liquid material there has from 1 to 20 links of the original unit, whereas the T-24 has material that runs all the way up to 150 links.

XQ. You have said that the liquid material has so and so. Would it be accurate also to say that the resinous material has so and so, of T-24-A? A. Yes.

. . . . . .

[308] XQ. Now, T-25-A was the less viscous alkyd resin portion of the G-25. What is the molecular weight of that less viscous alkyd resin portion? A. The weight average molecular weight of Exhibit T-25-A is approximately 10,000, which means that in that liquid material there are from 1 to approximately 36 links of the original unit.

XQ. Now when Dr. Rathman fractionated the samples, what method did he pursue? Would you state it in reasonably simple terms so I can understand it and it will have to be simple?

. . . . . .

[309] A. The way they are separated, it is in just the reverse order of what you just stated. The higher molecular weight material comes out and then as you go along progressively the material of lower molecular weight tends to separate out until finally you are left with the material of the low molecular weight, which formed the liquid fraction.

XQ. Well, it goes along progressively, so to speak; some heavy material comes off, and then some more, and then some more, and so on? A. Yes.

XQ. So, in fractionating, you can divide the material into any sized fractions you desire, can you not? A. Yes.

XQ. You can get a fraction of fifty per cent, the heavier material, and then take that and what is left is fifty per cent of lighter material? A. Yes.

[310] XQ. And then you can take off twenty per cent of the heavier material, on that side, and then what is left is eighty per cent which is lighter and less viscous? A. Yes.

XQ. Now, with the G-25, Dr. Rathman chose to stop, or to proceed to cut off eighty-eight per cent of what he terms, as I understand it, what he would term, the heavier or more viscous resin, and then twelve per cent of the less viscous resin fraction; is that right? As I remember it, those were substantially the percentages, eighty-eight and twelve. A. Yes.

XQ. And, with the G-40, Dr. Rathman chose to progress a little further, I gather, until he had taken off approximately sixty-seven per cent of what is termed the heavier fraction, leaving thirty-three per cent of the less viscous resin of the original material. Is that not so? A. Yes.

XQ. Now, he might, with the G-25 he might, have chosen to have the same ratio of sixty-seven to thirty-three, if he had chosen, might he not? A. Yes, he might have, but it is unlikely that he would have, because I asked him to separate the liquid [311] fraction of low molecular weight from the original Paraplex G-25 and the Paraplex G-40. Now I mentioned earlier that the Paraplex G-40 has a molecular weight distribution which indicates that there is a much greater quantity of low molecular weight material present, that is, a much greater quantity of liquid ester material of low molecular weight present in the Paraplex G-40 than there is in the Paraplex G-25.

XQ. Well, he might have chosen different fractions for each had he desired; that's all I wanted to know? A. I don't know what he might have chosen. I told him to separate the liquid material from the Paraplex G-25 and the liquid material from the Paraplex G-40, and that is what he did.

XQ. Did you tell him what your standard of the vague

and broad term "liquid" was? A. I don't recall that I indicated to him any standard for "liquid," no, sir.

. . . . . .

[313] A. The ester generally does have an ester chemical structure.

XQ. And, yet, it is termed an ester, regardless of what the constituent elements, what the chemical compound is; whether it's a solid, or a liquid, or whether it's an oil, or whether it's a wax, or whateyer it is, it would still have the chemical structure termed an ester; is that not so; it may still have the chemical structure termed an ester? [314] A. An ester is the chemical combination of an organic acid and an alcohol, that is, a hydroxy compound. Now esters may be liquid or they may be solid, depending—

. . . . . .

The Witness: Yes, esters may be a gas, under certain temperature conditions and atmospheric pressure—certain pressure conditions.

XQ. (By Mr. Holmes) Well, the term is so broad, then, is it not, as to include literally millions of widely different chemical compounds, each one of which could be referred to as an ester; is that not so?

. . . . . .

The Witness: Yes, it can refer to a broad class of materials.

. . . . . .

[315] XQ. Does the term "ester" encompass, to use some homely examples, such widely different compounds or materials as acetate rayon, photographic film? A. Cellulose acetate is an ester. Photographic film may be an ester or not, depending on what you mean by photographic film.

. . . . . .

A. Vinyl acetate is an ester.

. . . . . .

[316] XQ. Is T-24, which is the heavier, more viscous fraction of G-40, an ester plasticizer? A. It is chemically a polymeric ester plasticizer that is non-migrating in character.

XQ. So it is an ester plasticizer, using that term in its broad classification as we have been using it so far, as having an ester chemical structure? A. It is what they call a linear polyester plasticizer, yes.

XQ. And it could be termed an ester plasticizer? A. Yes.

[317] XQ. If you wanted to be more precise, you would call it a polyester plasticizer? A. Yes.

XQ. But it is an ester plasticizer? A. Yes, it would also qualify for that description.

XQ. So esters, in relation to plasticizers, may be of a migrating liquid type, or they may be of a non-migrating resin type? A. Yes. The liquid portion of Paraplex G-40 is properly called an ester, and the higher molecular weight portion may be properly called an ester plasticizer.

XQ. And the liquid type of migrating plasticizer, such as DOP, may properly be termed an ester plasticizer? A. DOP is an ester plasticizer.

XQ. Now this particular classification, as I understand it, of esters has been divided into, for purposes of more precise identification, into monomeric esters and polymeric esters; is that not so? A. There are monomeric ester plasticizers. DOP is an example of an ester plasticizer where the individual units of the plasticizer are all composed of the single chemical compound DOP; in other words, you do not have two, three or more units chemically linked together. You also have in Paraplex G-40, for example, which [318] is a plasticizer, you also have esters that are linked

together as is the case where polymers are present, as is the case in the Exhibit T-24.

XQ. And when those monomers are linked together by polymerization, the product, such as G-40, is termed more specifically a polymeric ester; is that not so? A. Yes.

[319] XQ. So T-24, T-24-A, T-25, T-25-A are all polymeric esters. Is that not correct? A. They are all polymeric esters.

. . . . . .

XQ. And you referred to the heavier portions of the fractions as the portions or fractions of these polymeric esters as viscous resin plasticizers. Now, why did you refer to T-24-A as an ester plasticizer and T-24 as a resin plasticizer? A. Because that is what they are.

. . . . . .

XQ. And with equal accuracy you could have called T-24 an ester plasticizer. Is that not so? A. T-24 is an ester plasticizer of very viscous character because it is polymeric.

. . . . . .

[320] XQ. And when you call T-24-A an ester plasticizer, you do not distinguish it in any way from DOP? A. That's right, they are both properly called ester plasticizers, and they are both liquid and both of low molecular weight as contrasted to the material of Exhibit T-24, which is the soft, viscous resinous portion of higher molecular weight Paraplex G-40.

XQ. By calling T-24 a resin plasticizer, you do distinguish it from a liquid type DOP do you not? A. DOP is generally not called a resin.

XQ. Is it ever called a resin? A. No it is not, not that I have ever come across.

XQ. So if you want to distinguish T-24-A from DOP, you

do, and you have in this testimony, called T-24-A a resin plasticizer? A. It is a liquid ester plasticizer.

. . . . . .

[321] XQ. But that term, liquid ester plasticizer doesn't distinguish it from DOP. Anyone reading the words "liquid ester plasticizer" might think that could refer to DOP. Is that not so? A. There was no additional distinguishing adjectives used in that connection because both DOP and the liquid material of Exhibit T-24 are properly called liquid ester plasticizers. Now, the material of T-24-A may also be called a resin because it is a resin, and it is also liquid and it is also an ester, and it is also of low molecular weight as contrasted to the very viscous fraction of the origina.. Paraplex G-40, namely, Exhibit T-24.

XQ. Well, I just wanted to be sure that anyone reading this wouldn't think that the T-24-A was being termed a liquid ester plasticizer; would think that it was a liquid type [322] migrating low molecular weight plasticizer such as DOP. That's all I wanted to make sure of. Now, when you mix T-24 and T-24-A, the more viscous and the less viscous fractions—resinous fractions of G-40, you restore the G-40 to the product you started with do you not? A. Yes, when you put the material of Exhibit T-24-A, namely, the two ounces of liquid material comprising the low molecular weight ester with the four ounces of viscous resin of materially higher molecular weight that is represented in T-24, you obtain six ounces of Paraplex G-40 of identical composition to the Paraplex G-40 as it is sold by the Rohm & Haas Company.

. . . . . .

XQ. Well, when you restore those fractions, put them together, you then have a non-migrating high molecular weight resin plasticizer? A. You have a non-migrating plasticizer which has a majority [323] of the material pres-

ent that is of high molecular weight, along with material that is liquid and of low molecular weight.

. . . . . .

[331] XQ. Now, is the resinous plasticizer G-25, a phthalyl ester? A. It is not.

XQ. Is the resinous plasticizer G-40 a phthalyl ester? A. It is not.

. . . . . .

[332] XQ. Did I understand you to say this morning, Mr. Tierney, with regard to T-24-A, that it had molecules of from one to twenty units or links? A. Yes.

XQ. And that T-25-A has molecules of from one to thirty-six units or links? A. Yes, sir.

XQ. Do you agree that you previously testified that [333] the lowest molecular weight in G-40 was a thousand? A. I may have said that, yes.

XQ. Then will you also agree that the unit of G-40 is about 174, or thereabouts? A. No, I will not agree to that. The individual unit of G-40, which constitutes the combination of adipic acid with two molecules of propylene glycol and the resulting elimination of two molecules of water, yields a unit that is 262, which is the molecular weight of the one unit of G-40 that may combine together with other units in making the polymer of increasing molecular weight in the polymeric material.

. . . . . .

[334] XQ. Your unit value was 262? A. Yes, that is the original unit of the reaction between adipic acid and two molecules of propylene glycol to form the di-glycol, di-propylene glycol adipate.

XQ. And dividing the 262 into a thousand we get approximately four? A. Yes.

XQ. And wouldn't that indicate, then, that the minimum length of chain was four or more, to a chemist? A. It

would. If I said that the Paraplex G-25 and the Paraplex G-40 was one to fifty thousand, I was giving the approximate range by molecular weight that is present. I will say that there may very well have been a small portion that would be from five hundred to fifty thousand.

XQ. But you don't suggest that there was a portion of monomer in there? A. There might be a very small portion of the original single unit present; it would be very small.

XQ. And you really mean very small? A. Yes.

[335] XQ. Such as would normally go out in a finishing operation of the material? A. I would say that it is present to the extent of less than one per cent.

. . . . . .

XQ. Is there any evidence of any monomer in the G-40 that you have ever seen or heard of? A. I, personally, have not found any, but I, personally, have not fractionated the G-40 or the G-25 with the express aim of attempting to determine whether there is any monomeric unit present of the reaction product of adipic acid and propylene glycol.

XQ. Now, passing to T-25-A, did you say that it has units from one to thirty-six or more? A. That was Exhibit T-25-A?

. . . . . .

[336] XQ. And what do you say as to the unit of 222 for G-25; will you accept that? A. No.

XQ. What is your figure, then? A. The molecular weight of the one unit of di-propylene glycol sebacate is 318.

XQ. And if we divide that into the one thousand which you gave for the minimum molecular weight of G-25, we come out three plus, do we not? A. There again if, in my previous testimony, I said one thousand to fifty thousand, I was giving an approximate range, and I repeat that in that instance also there might very well be from 318 to fifty thousand; namely, there might be some monomeric, single-unit

material representing the reaction product of sebacic acid and two molecules of propylene glycol, or, namely, the dipropylene glycol sebacate, which has a molecular weight of 318. There would be a very small amount of it, because there is a small amount even of the material that runs up to a weight average molecular weight of ten thousand. As you can see, the total amount of that material that is present in [337] the Paraplex G-25 of a molecular weight, that is, weight average molecular weight, of ten thousand or less down to 318 amounts to only twelve per cent of the Paraplex G-25 of current vintage. Now these fractionations were made of the Paraplex as of 1955 manufacture and sale.

XQ. In your opinion, in either G-25 or G-40 is there any significant separate amount of monomer? A. I don't know. . . . I will agree that the amount is small and undoubtedly is less than one per cent of the material as it is now being made by Rohm & Haas Corporation.

. . . . . .

[339] XQ. Is it your position that the old G-25 had more than a fraction of one per cent of the monomer present? A. No.

. . . . . .

JOHN M. DEBELL, witness on behalf of defendant:

Direct Examination.

. . . . . .

[417] A. I was graduated in 1917 from the Massachusetts Institute of Technology with the degree of Bachelor of Science in Chemical Engineering.

Q. Will you please state what your activities, occupations and experience have been since your graduation from Massachusetts Institute of Technology? A. The first two years after graduation I served with [418] the Armed

Forces of the United States; from 1920 to 1922 I was Assistant at the Massachusetts Institute of Technology to the Director of the Division of Industrial Cooperation and Research; from 1922 to 1932 I was employed by General Electric Company at Pittsfield, Massachusetts, where I was in charge of development and later manufacturing of two types of synthetic resins and molding compounds, including the alkyds and phenolic materials; from 1932 to 1936 I was a group leader at Hercules Powder Company, of Wilmington, Delaware, and during that time I introduced ethyl cellulose, a plastic material, into the United States; from 1936 to 1939 I was Director of Research and Development for the Fiberloid Corporation which, in 1938, merged with Monsanto Chemical Company and became the Plastics Division of that company; since 1939 I have been a consulting chemical engineer, working entirely in the plastics field.

. . . . . .

[419] Q. Since you left Fiberloid, what has been your occupation and experience? A. I have been a consulting chemical engineer in the plastics field. During the war I was consultant to the War Production Board, specializing in plasticizers, to the Office of the Quartermaster General and—

Q. Just a minute. Your War Production Board work did that concern not only plasticizers but polyvinyl compounds and so on? A. It did. And also to the Office of the Rubber Director, where again I specialized in plasticizers. In 1943 I set up a partnership, still in the consulting engineering field, which was incorporated in 1946 as DeBell & Richardson, [420] Incorporated, and that has continued to the present.

Q. How much of a staff does your laboratory have? A. We have currently about fifty people, of whom, roughly, one-half are graduate engineers or chemists.

. . . . . .

The Witness: It does experimental work and consulting solely in the plastics field, plastics including polymeric materials, modifiers, compounds, and processes, and equipment for those processes.

. . . . . .

Q. Do you design plants for making vinyl resin products? A. Yes, and for making the resins themselves.

[421] Q. Have you been the consultant for the major plastic and chemical companies in this country? A. Yes, broadly speaking, I think practically all the major ones with the exception of duPont and Carbide.

. . . . . .

Q. Are you the author of any work, scientific work, on plastics? A. Yes. Aside from magazine articles, I wrote, with Mr. Goggin, of Dow Chemical, and Mr. Gloor, of Hercules Powder Company, the comprehensive record of the German plastics industry entitled "German Plastics Practice."

Q. Did you tell me that at one time the Government sent you to Europe for this purpose of this book? A. Yes.

. . . . . .

[423] Q. And were the chemical properties and other properties of plasticized vinyl compounds well known in the thirties? A. Yes.

Q. Including the insulation quality? A. Yes, they were.

Q. Were they known to have high dielectric strength? A. Yes. That was a factor in their use in cable insulation.

Q. Water resistance? A. Yes.

Q. Oil resistance? A. Yes.

[424] Q. Resistance to weather and sunlight, and so on? A. Yes, reasonably good, especially if pigmented.

Q. And resistance to chemicals, gasoline? A. Excellent chemical resistance, and especially toward the aqueous types of chemicals.

Q. That was all well known? A. That is right.

Q. Now reference has been made, and is made in the patent, I believe, to copolymers of vinyl chloride and vinyl acetate with a high vinyl chloride content. What is the significance of having the vinyl chloride content a high one? [425] A. When the vinyl chloride content is high, it has been found that the polymers of that composition give the greatest strength, toughness and resilience, especially in plasticized film. They also have a sufficient softening temperature.

Q. That was all known in the thirties? A. That is correct.

Q. So the high vinyl content is perhaps essential for such a product as a tape. Is that not so? A. That is correct.

. . . . . .

[426] Q. Is it desirable that the mixture of the vinyl with the plasticizer, or plasticizers, should be a homogeneous one? A. It is very important because the subjection to heat must be somewhat limited, the temperature must not rise too high, so that it is always customary to get as perfect a mixture as you can before the heat treatment, and then to mill sufficiently to get a completely homogeneous structure.

Q. And that was standard practise in the thirties? A. That is correct.

. . . . . .

[428] Q. Prior to the war, had any particular plasticizer for vinyl compound won its way as the preferred plasticizer? [429] A. Yes, DOP was a very much preferred plasticizer for polyvinyl chloride before the war.

Q. And would you say that the use of DOP had become more or less the accepted plasticizer, in practice? A. Yes, it was then and for many years after.

Q. Now what qualities does this preferred type of liquid plasticizer, DOP, have that made it particularly desirable? A. DOP is a good solvent, that is, a good plasticizer. It has good solvent power for polyvinyl chloride. It has very low volatility; it maintains good flexibility in films at quite low temperatures; it has good color; it is not particularly toxic; and it is comparatively low in cost.

Q. Is it easy to incorporate into the material? A. It incorporates very readily.

. . . . . .

[429] Q. Was it known—I don't know whether I have asked you this before—that all liquid plasticizers were migratory? A. Yes.

. . . . . .

[430] Q. The Oace patent, column 2, line 41, refers to "liquid type plasticizers" and in column 3, line 30, it refers to "rosinous type plasticizers". As thus defined by Oace, are these two types, two well recognized and defined, distinctive types of plasticizer? A. Yes they are, and they are quite well defined by Oace himself in his examples. For example, on liquid type plasticizers, he mentions in column 3, line 27, Dioctyl phthalate, and in column 5, line 7, tricresyl phosphate, and dibutyl phthalates and butyl phthalyl butyl glocollate. All these are liquid plasticizers, as that term was then generally used in the technology of this art. Those liquid plasticizers had many properties in common. They are all monomeric, that is, they are very simple, precise, well defined chemical compounds of molecular weights of the range from say 250 to 600 or thereabouts. They are thinly fluid. For example, you already have in evidence, and I have here a tube of dioctyl phthalate, and you can see that a bubble rises very rapidly through this plasticizer. It has a viscosity of less than one poise, the poise being a unit in which such

viscosities are [440] measured. It is so mobile as you can see that it is migratory. It is so liquid that it will move readily when given an opportunity. Furthermore, every molecule in this plasticizer is just like every other molecule, so that it cannot be fractionated.

Q. And what you have said as to the DOP, is that true of all the other liquid plasticizers? A. Those characteristics of monomeric structure, migration, low viscosity, low molecular weight,—

Q. Thinly fluid? A. Thinly fluid, apply to all the liquid plasticizers mentioned by Oace and also those which were customary in the trade.

Q. Now what does resinous type mean to you? A. Well, a resinous type plasticizer is a synthetic material made by combining chemicals to a very high molecular weight so that you obtain an extremely viscous plasticizer, the viscosity for example of this tube of G-25 which I hold before you is about a thousand poises. The molecular weight is very high, in the thousands, and it is quite variable because there are molecules, as you have heard in previous testimony, all the way from a thousand in size to 50,000 in size, and this, unlike the DOP or the liquid plasticizer, here is a great big, clumsy molecule, it is huge, it doesn't [441] move fast, and it doesn't migrate, and since it has variable molecular weight, it can be cut into fractions of different molecular weight and each one of those fractions can be further cut into more fractions, all of which are resin plasticizers, taken from the resin plasticizer with which you start.

Q. You say "variable molecular weight". Is it all high molecular weight? A. As I pointed out, it is extremely high molecular weight, well into the thousands.

Q. Are the resinous type plasticizers commonly called polyesters? A. Yes, they are properly so termed.

Q. Also are they properly termed polymeric? A. Yes they are polymeric.

Q. I think you have already stated, but I'll ask you, is the resin type a distinct well recognized type as meaning what you are saying, high molecular weight, viscous, non-migrating, material as distinguished from a semi fluid thinly fluid liquid type. Is that correct? A. It is.

Q. Would you say that in chemical parlance, and as particularly defined by Oace, the liquid type and the resinous type are two well known distinctive types which are mutually exclusive and do not overlap? A. That is correct.

. . . . . .

[447] Q. Is a resin type plasticizer, a liquid type plasticizer? Is that term used in these examples I am giving you? A. The resin type is not properly called a liquid type plasticizer, as we in the trade, and Oace, have defined it. It is quite true that as a state of matter, the resin type plasticizer is a liquid, a very heavy viscous liquid, which can in time be poured. However, it is so distinct in its properties from the liquid type plasticizers, that it is not properly described as a liquid type plasticizer.

Q. Can you properly describe any part of it as a liquid type? A. No. No matter how far it may be fractionated, all of the fractions partake in their properties of the typical resin type plasticizer.

Q. And are non-migrating? A. Non-migrating and high molecular weight.

Q. Now I think I heard, and I think perhaps you did in your testimony, referred to a liquid type plasticizer as monomeric. Is that correct? [448] A. Well yes, that is a proper designation and that means that it has one form, it is a simple precise molecule.

Q. Now on page 326 of the record Mr. Tierney stated that he did not understand what I meant by a monomeric

plasticizer. Do you understand what is meant by a monomeric plasticizer? A. Yes I do.

. . . . . .

[449] Q. And does the art understand what is meant by "a monomeric plasticizer"? A. Yes, it does.

. . . . . .

[451] Q. Now, is this classification which appears in this technical literature of monomeric, on the one hand, and polymeric, on the other, is that the same classification [452] really that is made by Oace when he refers to "liquid type" and "resinous type"? A. Yes, all the liquid plasticizers mentioned by Oace fall in the monomeric class, and all the high molecular weight polymeric types, examples, fall in the resinous class, or, rather, his resinous examples fall in the polymeric class.

Q. Well, the two classifications are parallel, monomeric and liquid, and polymeric and resinous; is that not so? A. That's correct.

Q. What is the significance of the word "ester," which has popped up in this case? A. "Ester" is a broad chemical term which signifies a particular type of chemical linkage. Practically everything, with the exception of vinyl isobutyl ether, practically all of the plasticizers, both liquid and resinous, of the Oace patent are chemical esters. However, in the trade, the term "ester plasticizer" came to mean sometime ago the liquid plasticizers, probably because of the historical order in which these plasticizers appeared and were used, so that the trade, by "ester plasticizer," ordinarily understands the liquid plasticizers of Oace, although it is quite true that almost every plasticizer in Oace has an ester structure.

Q. Has the art come to use "ester," the word "ester," as applied to plasticizers, exclusively to the monomeric type? [453] A. I would say largely. There are occa-

sional rare instances in which a publication will refer to ester plasticizers as something other than that, but in practically all cases the trade understands by "ester plasticizers" the liquid plasticizers we are here discussing.

. . . . . .

[455] Q. Do I understand that the term "polyester" means and is used to differentiate the high molecular weight resin type from the liquid ester type; is that correct? A. Yes, that's correct.

Q. I read from page 20 of the St. Paul depositions, our examination of Esther Eastwold, of the Minnesota Company, and I quote: "Q. What sort of plasticizer did you use?" "A. We used monomeric plasticizer and polymeric plasticizer." Was Mrs. Eastwold there, according to chemical usage, clearly defining the liquid types and the resin types of Oace? A. I would understand that she was referring respectively to liquid type and the resin type.

Q. What does "liquid phthalyl ester plasticizer" describe? A. The liquid phthalyl ester plasticizers are the simple monomeric esters of phthalic anhydride with a suitable alcohol, for example, DOP, dibutyl phthalate, diamyl phthalate, or materials of that kind.

Q. Are there liquid plasticizers which are not phthalyl? A. Yes.

[456] Q. Referring to the Oace patent, are the liquid plasticizers referred to in column 5, the first paragraph, of the ester type, as that phrase is used in the art and in the literature you have referred to? A. Yes, those are ester type plasticizers.

. . . . . .

Q. Does the patent clearly distinguish between liquid type plasticizers and resinous type? A. Yes, it distinguishes between them at the very be- [457] ginning of the description, in column 3, line 27 and line 29, and throughout

the patent there are constant references to this two-plasticizer system, the liquid plasticizer of column 3, line 27, and the resin type plasticizer, same column, line 31. The liquid plasticizers are detailed in column 5, the first paragraph. The resin plasticizers are detailed in the following paragraph. Further references to this two-plasticizer system are in column 5, line 16; in column 7, lines 5, 6 and 7; in column 7, line 16—

. . . . . .

Q. What is the teaching of this Oace patent, Mr. DeBell, to you, as a man familiar with this art? A. The Oace patent teaches that a two-plasticizer system makes a successful pressure-sensitive vinyl-backed tape. It overcomes the previous objection that all-liquid type plasticizers could not be used because they would interfere with the film, and it points out that all-resin type plasticizers [458] can not be used because they interfere with the film.

. . . . . .

[459] Q. Is there any statement, suggestion or intimation in this patent as you read it, that any resinous type of plasticizer can be used successfully as the sole plasticizer? A. I find no such suggestion, and in fact the patent warns against it. . . .

. . . . . .

[467] Q. Now, referring to G-40, I think you said that is a resinous type as distinguished from liquid type. Is every part and portion of G-40, of the resinous type as distinguished from a liquid type? A. Yes, it is.

Q. However fine you fractionate it, it is still viscous, nonmigrating, high molecular weight, high viscosity? A. That's correct.

Q. Now Mr. Tierney introduced two fractions of G-40, being T-24 and T-24-A. T-24-A, as I remember, was the slightly less viscous portion. Now is that portion of G-40

represented by T-24-A of the resinous type, high molecular weight, non-migrating plasticizer material? A. Yes. May I look at that?

Q. Yes. A. (Inspecting exhibit) Yes, that is a resinous plasticizer.

Mr. Holmes: I think these labels are a little misleading, Your Honor. It is called a liquid. But, then, I won't quarrel over that.

Will you please read the witness' answer back to me?

(The record was read by the reporter.)

Q. (By Mr. Holmes) And does it have the other characteristics I mentioned? [468] A. Yes.

Q. Is T-24-A, or any part of it, of the liquid type, or does it, or any part of it, partake of the characteristics of the liquid type of plasticizer? A. That is not the liquid type as defined here earlier by Oace, or by the custom in the trade. It is a resin plasticizer. It's high molecular weight, it's non-migrating; and we have confirmed those facts with our own fractionations.

Q. Does T-24-A, or any part of it, partake of the characteristics of liquid phthalyl ester plasticizer? A. No, it does not.

Q. Is T-24-A, or any part of it, of the ester type, as that phrase is used in the art and in the literature you referred to? A. T-24-A, as referring to the usage of the trade, is not an ester-type plasticizer. However, I would point out that it does have ester-type linkages, as do practically all the plasticizers, I think, save one, of all types which we have considered in this patent.

The Court: It is, though, of a fluid or liquid type, as distinguished from a powdered product, isn't it?

The Witness: It is liquid in that it is not a solid and is not a gas, but in this patent there is a clear definition—

. . . . . .

[469] The Witness: That's the basic difference between high and low viscosity. The low-viscosity plasticizers run like water; the liquid plasticizers run, as Mr. Tierney said, like water; the resin plasticizers run very slowly, some faster than others, but several hundred times as slow as the liquid plasticizers.

. . . . . .

Q. Now, Mr. Tierney stated that he instructed his laboratory experts or assistants to fractionate off the liquid portion of G-40, and the assistant came up with T-24 and T-24-A. [470] T-24-A being what Mr. Tierney terms, and this label terms, the "liquid fraction," being one-third of the total. I think I have already asked you is T-24-A a liquid plasticizer material, or is there any liquid portion in that material. A. There is no liquid plasticizer, as defined by Otace, . . .

Q. T-24-A is the fraction. If you were asked to fractionate off the liquid material of G-40, which, as I understand it, is what Mr. Tierney asked his assistant to do, would you know what fraction to take off, or would that mean anything to you? A. No, that would be meaningless. If I were saying that a liquid is something which will pour, something which will take the shape of the container, then that would mean I was to take off everything from everything. If the liquid part there refers to a liquid plasticizer, then, of course, those instructions would mean take nothing from this.

Q. Now is what you said as to G-40 true also as to G-25? A. Yes.

Q. That it is a high molecular weight, non migrating, viscous resin plasticizer in all its parts; is that true? A. That's correct.

. . . . . .

[471] A. You understand, Mr. Holmes, that in fractionation you can always take off any sized fraction or any number of fractions when fractionating a resin plasticizer.

Q. So there is no liquid portion in G-25, any more than there is in G-40; is that your conclusion? A. Well, it's a misnomer, for the reasons I have mentioned.

Q. Can a liquid plasticizer be fractionated? A. No.

Q. Could you get off any fraction of G-40 or G-25 which would fall within the category of liquid type, as Once used that phrase and as it is used in the art to which you have referred? A. No. We made attempt to do that by the distillation method, that is, under very high temperature, 260 Centigrade, and very high vacuum, 10 millimeters, which is one seventy-sixth of an atmosphere, the pressure now around us. We tried to distill off from G-40 something that would correspond [472] to a liquid plasticizer. Under those conditions, we had no difficulty in distilling DOP from a mixture of G-40 and DOP; there we could distil it off without difficulty, recover it and identify it. We were not able, under the same conditions, to get one single drop from G-40.

Q. If there had been anything comparable with DOP in the G-40, would it have come off? A. We would have gotten something off.

Q. Do you know about the conditions of manufacture of G-40 and G-25, which would insure no light material? A. I have not seen the manufacture of G-25 and G-40. I am familiar with the manufacture of alkyd resins and alkyd type plasticizers.

. . . . . .

The Witness: I said, sir, that I am not familiar [473] personally with the precise conditions under which G-25 and G-40 are manufactured. I am familiar with the conditions under which alkyd resins generally are manu-

factured, and we heard at Rohm and Haas, and I believe it is in the record, statements as to the methods used at the essential points of manufacture of G-25 and G-40. These details of manufacture were the same as are usual in alkyd resins; that is, the ingredients are heated to high temperature, above 150 Centigrade. The water of reaction goes off. When the acid number is down—you see, here are a great many acids that have to be tied up into a big molecule—when the acid number is down, then it's customary to strip the resin mass under high vacuum and suck off everything that's even remotely volatile. I might say also that this is always done in a nitrogen atmosphere so that oxygen doesn't get in the way. Now Rohm & Haas men stated in my presence—

The Court: Was that when the depositions were taken?

The Witness: Yes, sir.

The Court: Don't put anything in that's not in the record here.

The Witness: I will try not to, sir. When these plasticizers are vacuum-stripped—and I would say from our distillation test of G-40 that it must have been vacuum-stripped, because we subjected it to a drastic condition and [474] could not get a single thing off, under conditions where we could actually distil off DOP. I have the tubes here, if they are of interest.

Q. (By Mr. Holmes) Does T-24-A, which is the less viscous fraction of G-40, have molecules of from 1 to 20 units? A. No.

Q. As testified to by Mr. Tierney? A. Judging from Mr. Tierney's testimony, it might have molecules from 4 to some higher number of units. Actually, and from looking at the viscosities of these samples, I would be greatly surprised if there is as much as one per cent of any resinous material in G-40 that has a molecular weight below 2,000.

Q. Does T-25-A, which was the less viscous fraction of

G-25, have molecules of from 1 to 30 units, as stated by Mr. Tierney? A. Not according to Mr. Tierney's testimony. By simple arithmetic, that fraction could have no units smaller than—could have no fractions smaller than 3 to 4 units, no molecules smaller than 3 to 4 units.

Q. Mr. Kirkpatrick, in his cross-examination of Mr. Tierney, gave 174 as the unit for G-40, instead of 186. Is 186 correct for the unit of G-40? A. Well, I must take the blame for that. 186 is the [475] correct unit for G-40. If I said something else, I had figured it wrong in the hasty computation of the court-room, and perhaps a certain amount of indignation at trying to get some monomer in the picture, which I was quite certain was not present. 186, I believe, is correct, if my arithmetic hasn't faulted again.

Q. Do you remember what it is for G-25? A. I similarly think it is 272, but, in any case, the unit that is found, that is, the thing that corresponds to a monomeric unit in this great, big resin molecule, is one acid, either sebacic or adipic, hooked up at one end to one glycol. That is the basic structure of this unit, and that repeats hundreds of times in order to build up this big general molecule.

Q. In your judgment, is there any possibility that in G-25 or G-40 there is present any material that could be described as a liquid, migrating plasticizing material of low molecular weight? A. No, I believe there is no such material present, and we have confirmed that not only by the distillation test which I just mentioned, but also by fractionating off a lower molecular weight fraction and then making tests of that in tape against pressure-sensitive adhesives to see if that had any [476] of the characteristics of DOP. They had none. Where DOP, under the same circumstances, would stick mightily to the tape, these lower molecular weight fractions of resin plasticizers did not so

stick. They were, however, much easier to incorporate with the vinyl chloride.

[477] Q. Now Mr. Tierney gave the range of molecular weights of G-25 and G-40, from 1000 up. Does that range —is that range consonant with your observed facts? A. I would not question that range of I think from 1000 to 50,000. It sounds reasonable.

Q. Well, the fact that there is nothing lower than a thousand, does that in itself mean that there is no thinly fluid light molecular weight material there? A. That is correct.

. . . . . .

[479] Q. Mr. DeBell, on page 475 of the record of your testimony yesterday, at the bottom of the page, you stated that there was no such liquid migrating plasticizer material in G-25 or G-40 and you had confirmed it by certain distillation tests and also by fractionating off a lower molecular weight fraction and then making tests of that. Were those tests made in tape? Just answer "yes" or "no"? A. Yes, they were made in tape.

Q. And continuing; "Making tests of that against sensitive pressure adhesives to see if they had any of the characteristics of DOP, they had none," you state, and then you continue: [480] "Where DOP under the same circumstances would stick mightily to the tape, these lower molecular weight fractions of the resin plasticizer did not stick". Can you perhaps amplify that a little? Amplify it as to the deductions you draw from the statement you made? A. Yes, the tape which was made entirely with DOP showed so much migration that it was impossible to separate the adhesive tape and the vinyl tape cleanly, whereas when the lower molecular weight fraction of G-25 was similarly used, there was no evidence of migration and the adhesive tape peeled cleanly from the vinyl tape which we had made.

Q. And from that you deduce that there was not—was it G-40? A. G-25.

Q. Any such material as DOP. Is that correct? A. Yes, material which would function in tape like DOP.

Q. Mr. DeBell, on page 179 of the record Mr. Tierney testified that T-24-A, the less viscous fraction of G-40, is: "an liquid ester plasticizer". On the next page he described the more viscous portion of T-24 as "a soft viscous resinous portion". What do you have to say as to his finding one portion of G-40 as "a liquid ester plasticizer" [481] and the other as "the soft viscous resinous portion"?

. . . . . .

Q. Defining one portion of G-40 as "a liquid ester plasticizer" and the other or more viscous fraction as "the soft viscous resinous portion"? A. Well, I'm afraid that is grossly misleading because it would tend to confuse the lower molecular weight resinous fraction of one of these resin plasticizers with the liquid type plasticizer which has been so carefully defined by Oace. Both of those fractions which you mention, are resin plasticizers.

Q. And both are viscous resinous non-migrating high molecular weight resinous plasticizers? A. They are, and they are both capable of further fractionation.

. . . . . .

[482] The Court:

Q. You find fault with that and you say it is grossly misleading. In what particular?—A. Because it tends to confuse the resin plasticizer fractions with the liquid plasticizers. As Oace has clearly pointed out, he deals with a two plasticizer system, a liquid plasticizer and a resin plasticizer. No matter how much you fractionate the resin plasticizer, the fractions are still resin plasticizers and should not be confused with the liquid plasticizers.

. . . . . .

Q. Would you say it was equally misleading to refer to the T-24-A as counsel did on page 180, as "This liquid ester fraction"? [483] A. Well, it is unfortunate because of the same confusion which might arise.

. . . . . .

[486] Q. (By Mr. Holmes) By describing one portion, the portion T-24-A, as a "liquid ester plasticizer," does that description reveal that it is a resinous, soft, viscous resinous high molecular weight plasticizer material? A. No.

. . . . . .

[489] Q. Now is G-40 "a soft and viscous low-acid-number alkyd plasticizer resin," as defined in Claim 1? A. Yes.

Q. Is G-40 a "resinous type plasticizer," as referred to in the Oace patent? A. Yes, sir.

Q. Is it in its entirety a "resinous or high molecular weight modifier such as Paraplex G-25"? A. Yes.

Q. Is it a "resinous modifier," as referred to in the Oace patent in its entirety? A. Yes.

. . . . . .

[490] Q. Now, does the use of DOP, as taught by Oace, mixing it with a resin plasticizer, have advantages? A. It has several advantages. In the first place, the resulting composition is much easier to process, the softening effect of the plastic mass is much better. Where DOP is used the total amount of plasticizer to produce a desired effect is less, and, of course—

Q. Why is that? A. Because the DOP has a higher solvent effect and confers greater flexibility on the polymer; and, of course, DOP has always been a cheaper plasticizer than the resin plasticizer.

. . . . . .

[491] Q. You have referred to certain advantages in the use of DOP, as taught by Oace. Are those advantages supplied by G-40, or any part of G-40? A. No. G-40 has approximately the same viscosity as G-25 in the samples, the random samples, which we have from Rohm & Haas and would present somewhat the same difficulties. It is a little easier to process than G-25, but not as easy to process as it would be if it were mixed with DOP.

Q. And you have to use more of it to get the same result? A. Of G-40 than of a mixture of G-40 and DOP.

Q. When you mix DOP with G-40, let's say, do you change the molecular weights of the molecules of G-40 in any way? A. No, there is no chemical reaction.

Q. Does G-40, because of its average molecular weight of around six thousand, instead of the average molecular weight of eight thousand of G-25, have any of the properties of DOP because of this lesser average molecular weight? A. No. That average molecular weight results from about the same degree of condensation of the molecules when the shorter adipic acid is used in G-40 as against the longer sebacic acid in G-25.

. . . . . .

[493] Q. At pages 149 and 151 of the record—and I will try to paraphrase this—Mr. Tierney testified that . . . if the specification range of G-25 had been narrowed there would be less tendency for higher molecular weight material to exude to the surface; and the elimination of these higher molecular weights would result in less tendency to exude or spew out.

What have you to say to that, Mr. DeBell?

. . . . . .

[494] The Witness: As I recall those remarks and the testimony, that was a speculation that in the early manufacture of G-25 there may have been additional high molecular weight resinous material which was of such high molecular weight that it would account for the effect which Oace speaks of as losing tack, and that the speculation further was that the early material may have had extra high molecular weight ingredients or fractions which were not present in the later material. To check that, we had samples in our stockroom of G-25 produced, first, in 1945; another sample produced in 1951; and current samples of production. We checked the viscosity of those samples both against the bubble tubes and in 50 per cent solution. The viscosity of the earliest sample was the lowest of the lot; the second sample—

[495] Q. That is the 1945 sample? A. The 1945 sample. The viscosity of the 1951 sample was next, and the viscosity of the present day sample was the greatest, although they were all of the same general order of magnitude; and from that it is clear that the speculation that the earlier materials had a very high molecular weight, extra high molecular weight fractions, is not correct. Those samples of the three lots have been included in this set of bubble tubes in the order of the viscosities in which they occur.

Q. Perhaps you will show that to His Honor, if he cares to see it, and what it demonstrates. A. This tube, Your Honor, is a sample of—

The Court: How have you got it designated there?

The Witness: This tube is designated "G-25, Lot 5466," which was made in 1945; "G-25, Lot 12-4316," which was made in 1951; and "G-25, Lot 12-5471," which is the current material which we purchased since this suit started.

[496] (By Mr. Holmes) Were these lots taken at random for your sample? A. They were just what we happened

to have in the stockroom, sir. You will notice, as I turn the tubes, that 5409 is slightly less viscous—

Q. That is the 1945? [496] A. Yes—that 12-4316 is slightly more viscous—

Q. That is the 1951? A. (Continuing)—and the 12-5471 is still more viscous, although in all cases the bubbles rise slowly.

Q. What are the other tubes there? A. While these are rising, the other tubes in this set are, first, a Gardner A standard viscosity tube, which has a viscosity of one-half poise; second, a dioctyl phthalate tube, where the viscosity appears to be of the same order of magnitude; third, a Gardner C tube, which is about six-tenths poise; next a Gardner Z-6 tube, which has a viscosity of 148 poises; next, a Gardner Z-7 tube, which has a viscosity of 388 poises; next the tube of G-25, Lot 5409, which has about the same viscosity, which has a viscosity between Z-7 and Z-8; next a Gardner Z-8 tube, which has a viscosity of 590 poises; next a Gardner Z-9 tube, which has a viscosity of 855 poises; text G-25, Bot 12-4316, which has a viscosity—

Q. What vintage was that? A. That is 1951, which has a viscosity, in my estimation, of around 950 poises; next a Gardner Z-10 standard tube, which has a viscosity of 1060 poises; next a current lot of G-25, Lot 12-5471, which I would estimate to have a viscosity of well over 1060 poises, somewhat over a thousand and sixty- [496a] six poises; and, finally, a current lot of G-40, lot 12-6216, which I would estimate to have a viscosity in the neighborhood of eleven hundred poises.

Q. Did you state what the viscosity was of the 1945 G-25 material? A. I'm not sure, but it appears to be in the neighborhood of four hundred to four hundred and fifty poises. . . . Now we have confirmed these viscosities by other types of measurements in ethylene dichloride solution [497] but the point here is that, from the samples

which we happened to have around, there is no indication that the early vintage of G-25 had substantial fractions of higher molecular weight material which would increase the viscosity.

. . . . . .

[498] Q. (By Mr. Holmes) Do you conclude that there has been no change in the specification range of G-25 from 1945 to date? A. No. I conclude specifically that the speculation that the earlier samples may have had higher molecular fractions than the later samples is incorrect.

Q. And would you conclude that there had been a significant change in the viscosity range of G-25 over the period? A. That, in my opinion, is correct.

. . . . . .

Q. Now, what is polymerized ethyl acrylate? This witness refers to it as a high molecular weight plasticizer material. A. Polymerized ethyl acrylate is the product which is obtained when the monomer, ethyl acrylate, is polymerized to a high molecular weight material.

[499] Q. By polymerizing it to a high molecular weight material, would you in normal process of manufacture, as these things are manufactured, produce a resin type plasticizer? A. Yes.

Q. And would all parts of such product be a resinous type? A. Yes.

. . . . . .

Q. Referring to this ethyl acrylate which he produces he states: "The composition that it has is controllable by [500] the organic chemist, the polymerization chemist tailors it to produce the ethyl acrylate polymer resin of the properties that he wants for the purposes involved". A. That is a correct statement, and the tailoring means by varying the conditions of the polymerization, for example

ple, the concentrations, the method of polymerization, the time, the temperature, the catalyst and other factors, different types of polymer can be produced as desired.

Q. Can the monomers be retained by such a tailoring, with ethyl acrylate? A. If the polymerization is not carried to completion, and if the product is not stripped, there will be monomer in the product.

Q. Now what sort of material is the ethyl acrylate monomer? A. Ethyl acrylate monomer is a volatile solvent. It has a boiling point I believe in the vicinity of 100 degrees Centigrade, about like water.

Q. Does it have a characteristic smell? A. Yes.

Q. Is it like DOP, a monomeric plasticizing material? A. No. It is monomeric but it is not a plasticizer.

Q. What would be the order of molecular weight of the [illegible] ethyl acrylate unpolymerized? Would it be lower than DOP? A. I would say offhand about a hundred, but it's in that book right there. I have not figured it. Reading from the handbook of Chemistry and Physics, the 32nd Edition, Ethyl acrylate is recorded as having a molecular weight of 100.11 and a boiling point of 99.8 degrees Centigrade.

Q. Would that be about like water? A. Yes.

Q. Did you take a piece of tape which Mr. Tierney had had made from this tailored ethyl acrylate? A. I did.

Q. And did you test it, and what did you conclude from your test? A. We took a sample of the tape from the Exhibit here—

The Court: Is that Exhibit 14?

Mr. Holmes: That's right your Honor, Exhibit 14. You have a remarkable memory.

A. I noticed a rather pronounced odor of ethyl acrylate, so we exposed a sample of that tape in an oven at 105 degrees Centigrade, to note the weight loss. We found that there was a very rapid loss within 24 hours, of 35

of the total weight of the tape, which would be of the order of the magnitude of 5%—of 5 parts per hundred of the vinyl chloride polymer used, as I recall that tape described by Mr. Tierney.

[502] Q. What did the odor indicate? A. Well, the odor indicated ethyl acrylate, and the oven test indicated the presence of a substantial amount of a highly volatile material. From that it appears that when taken in conjunction with the testimony as to what this sample T-14 was, that the plasticizing system there was composed of about 45 parts per 100 of a resinous polyester ester plasticizer and about 5 parts per 100 of a volatile solvent.

Q. Would the solvent have any plasticizing effect? A. It is momentarily plasticizing, but it is not a plasticizer because it disappears promptly.

Q. Would it aid in formulating the backing? A. It would aid in processing it.

Q. How would you define this tailored ethyl acrylate? As a mixture of what? A. Judging from the tape sample which we examined, and assuming that that was made from the polyethyl acrylate, and that no ethyl acrylate monomer was added, I would judge that the polyethyl acrylate was a mixture of the resinous polymer with a volatile solvent, the latter in small amount.

Q. Now this tape sample which you took of T-14, would it lose stretch? A. I don't know that we checked that loss of stretch, but it was very inferior to the regular tapes. Regular [503] tapes will stretch readily, 100%. We only had an elongation with this tape of about 55% to 60% when it broke.

. . . . . .

[505] Q. Is G-20 compatible with polyvinyl chloride? A. In ranges useful for flexible composition, no.

Q. Have you tried it? A. Yes.

Q. With what result? A. We tried to prepare samples

of 100 parts of VYNS and 43 parts of G-20. We were not able to prepare films from this combination. The incompatibility is quite obvious when you examine the sample. For the purposes of these tapes, G-20 is a useless plasticizer.

. . . . . .

[507] Q. Now, how about the tape which Mr. Tierney produced which he said was made with the use of G-20 as one of the plasticizing elements? How is that consistent with your statement that G-20 is not compatible with polyvinyl chloride? [508] A. That tape, as I recall it, consisted of 100 polyvinyl chloride resin, 24 G-20 and 24 Dioctyl phthalate. The normally incompatible G-20 was successfully pulled into this tape combination by the use of the excellent plasticizer DiOctyl phthalate. Was it Dioctyl phthalate? It is a well known practice in the vinyl art to use so-called extender plasticizers which in themselves are not suitable for a good product but which can be brought into solution by the use of a substantial proportion of a really good plasticizer, as was done in this case. You will notice also that the 24 parts of liquid plasticizer specified here, carries that tape out of the range of the Oace patent which limits the liquid plasticizer to 20 parts per 100 or thereabouts.

Q. By limit, you mean safe limit. Is that it? A. Yes.

Q. Maximum limit? A. Yes.

. . . . . .

[512] Q. Would the presence of a film of oil on the G-25 plasticizer in your judgment, have any deleterious effect on its utility as a plasticizer for the backing of this vinyl tape? A. No. I would expect it to function as a small amount of additional lubricant to the stearate which is already in the tape.

Q. Did you make tape from the 1945-G-25 as the sole

plasticizer, and with the 1951 G-25 as the sole plasticizer, and with current G-25 as the sole plasticizer? A. We did.

Q. What proportions did you use in each case? [513] A. We used 100 parts by weight of vinyl resin and 43 parts by weight of the G-25. I beg your pardon. We used 100 parts by weight of VYNS and 50 parts by weight of each of the G-25 samples respectively, plus a small amount, 3.5%-3.6% of calcium stearate.

Q. That's the stabilizer? A. As the stabilizer and lubricant.

Q. Now, what results did you observe as to these tapes? A. None of these tapes lost tack when exposed against the pressure-sensitive face of vinyl backed pressure-sensitive adhesive tape.

Q. Over how long a period did you test? A. Initially for a week and now for over ten days.

Q. If there had been a loss of tack it would have appeared in that experiment. Is that so? A. Yes.

. . . . . .

Q. Wait a minute. In making that test were you trying to follow the example 1 of the patent? A. We were trying primarily, sir, to check the statements of column 3, the paragraph beginning with line 45, and column 7, beginning at line 38. The methods used were similar to but not precisely like example 1. We prepared the film in [514] essentially the way they are described, but then we merely rolled that film down against another pressure-sensitive adhesive tape to see what effect the film would have on the pressure sensitive adhesive. In other words, we took from the market a primed tape which had a commercial type of pressure-sensitive adhesive on it, and stuck it on the film which we had made and observed whether there was any loss of tack between the film which we had made, which contained the G-25, and the pressure-sensitive adhesive on the commercial tape.

Mr. Holmes:

Q. Do you happen to know what brand of commercial tape you used? A. Yes. That was from a roll of Plymouth plastic electrical tape which was purchased by me on September 13, 1955.

. . . . . .

[515] Q. Now it was testified, on page 301, that G-40 has "a far larger quantity of lower molecular weight material than is present in Paraplex G-25". Do you agree with that statement? [516] A. Such fractionation and viscosity studies as we have made on the samples we have, do not confirm that. In general we would conclude that the proportions of relative molecular weights and the molecular weights of the products themselves, are not too far apart.

. . . . . .

Q. . . . It was testified on page 264: "That Paraplex G-40 has both the low molecular weight liquid plasticizer present in it, along with the high molecular weight resin plasticizer." Do you agree with that statement?

. . . . . .

[517] A. I do disagree sir. All the fractions of G-40 are high molecular weight resin plasticizers, and they should be so described to distinguish them from the totally different class of materials, the liquid low molecular weight plasticizers. The low molecular weight liquid plasticizer described by Oace in column 3, line 26—

. . . . . .

Q. Now on page 201 of the record, it was testified: "You have some material in Paraplex G-25 that would be identical to DOP in its viscous character." Do you agree with that statement? A. No.

. . . . . .

Cross-Examination.

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[575] XQ. Well, would you tell us how you can have any basis for an opinion as to what is the lowest molecular weight component in either of those? A. That basis arises from several observations. First, that the lowest molecular weight fraction that we have ever seen from our own work or from Mr. Tierney, or anywhere, still is a high molecular weight resinous material whose viscosity is so high, even when it's only 10% of the total fraction, that there is no particular indication of low molecular weight material. Second, I would accept Mr. Tierney's observation [576] that the lowest molecular weight fractions he ever found in G-25 or G-40, had molecular weights of a thousand. Third, if they were low molecular weight materials of the order of molecular weight, for example, of DOP, they should submit to ordinary physical means of removal. Now, we tried to remove such materials, as I pointed out, by high temperature, high vacuum distillation. We didn't get them. We also tried to check them by volatility from films, and again there was no evidence at all of the loss of any low molecular weight material.

XQ. Let's stop there a minute. High temperature, high vacuum distillation is not the way to go about separating these things, is it? A. It is an excellent way to see whether you have any Oace liquid plasticizer or anything like it in the material.

. . . . . .

[578] XQ. So, when you subject such a material to a high temperature vacuum distillation and get out no molecular weight, no low molecular weight material, it just doesn't prove one single solitary thing as to whether it's in there or not, does it? [579] A. Why of course it does.

It proves not only that it isn't there, but by any possible conceivable ester interchange reaction which you could have, that you couldn't even make it. It just proves that it isn't there and there is nothing there from which such a material could be made.

. . . . . .

[585] XQ. (Continued) Now you will notice there that in your answer you spoke about Mr. Tierney saying that there might be molecules of from four to some higher number of units? A. Yes.

. . . . . .

A. The arithmetic there was that if the smallest observed molecular-weight fraction is 1,000, and if the building unit is, let's say, 250, or 270, then the smallest [586] significant molecular size would be 1,000 divided by about 270, which equals 4, approximately.

XQ. So that answer was predicated on the belief that Mr. Tierney had said that the smallest molecular-weight unit in there was 1,000; is that correct? A. My recollection is that there was the remark that he had found molecular-weight fractions from 1,000 to 50,000.

. . . . . .

XQ. Anyhow, it was on the basis of Mr. Tierney's statement, which you have recollected as you just stated, that led you to say that by simple arithmetic there could be no fraction smaller than 3 to 4 units, numerically smaller than 3 to 4 units; that was your basis, wasn't it? A. Yes.

XQ. And your only basis? A. No. That confirmed a great many examinations which I had made of the product, all of which indicated that there is no detectible, at least no practical, amount of low molecular weight material of the order of magnitude of 4 to 5 in molecular weight, let's say, in G-25 or in G-40, which is further confirmed, and you can

readily, by doing [587] some computation on the acid-number, which is a matter of record and specifications.

. . . . . .

[611] XQ. Well, I just want to be sure I understand you. You do take issue then with Dr. Beavers in that statement? A. No. Dr. Beavers says he doesn't know, and I agree with him if he says he doesn't know.

The Court:

Q. If I understand you, you think you do? [612] A. That is correct sir, because I have performed the experiments which are here in the record, which teach me that.

. . . . . .

[613] XQ. I didn't make my question quite as close as I might have. Have you ever added the monomeric portion of G-40—to G-40 and then tried to strip it out by vacuum stripping?

. . . . . .

[614] XQ. Well, I'm talking about your adding what I understood you were calling the monomers, the one that had just one unit in it, not recurring units of the same thing? A. I don't think I referred to it as the monomer. I will now refer to it as a building unit and again define it as the reaction product of either—one molecule of either adipic or sebacic acid, with one molecule of glycol, to form a hydroxy acid which has one ester linkage, and going further to answer your question, I have not prepared that material nor added it to G-25 or G-40.

XQ. And if you did that, according to Flory's equation, you couldn't separate it out by fractional distillation vacuum stripping, could you? A. If I did that I would not be able to separate it by high heat and vacuum because it would immediately react in under the conditions of reaction, to become a high molecular weight material, and that

is shown clearly by contemplation of the acid number of G-25 and G-40 as furnished.

. . . . . .

[615] XQ. Let's come back to your answer of a moment ago where you said if you put some of this single building unit material into the Paraplex G-40 and tried to remove it by high temperature vacuum stripping, you couldn't remove it because it would polymerize. Is that right?

. . . . . .

A. What would happen, it would react.

XQ. It would react and you wouldn't get it out? A. Surely, and that's another reason why there can't be any monomer there.

XQ. Now wait a minute. I don't want us to be pulling [616] ourselves up by our boot straps. I understand that if you put some in and tried to remove it by vacuum stripping, you would not get it out because it would react? A. That's right. You would be making more G-25 and G-40.

. . . . . .

XQ. Well now Mr. DeBell, correct me if I misunderstood your direct testimony, but in your direct testimony I understood that you made a vacuum, high temperature vacuum distillation of Paraplex G-40, and you were unable to get anything out that way, and you therefore offered the conclusion that it had no monomeric material in it. Was [617] that your testimony? A. I offered the conclusion that it had no volatile materials in it in any way comparable to DOP, or more broadly, the liquid plasticizers of the Oace patent.

XQ. Well now, so we don't get mixed up in terminology, you do not consider the monomer of G-40 to be comparable to DOP in your terminology do you? A. Not precisely, because it is the reaction product of two truly monomeric materials, that is, the building block of G-25 and G-40, is

the first reaction product of two monomeric materials, which in this reaction, has only transitory existence.

XQ. Now coming back to your direct testimony that I'm trying to get to, do I understand that all you meant to tell the Court there that was shown by your high temperature vacuum distillation attempt of Paraplex G-40, was simply to prove that there was no DOP in it? A. No. It was to prove that there was nothing of the liquid plasticizer nature in it as defined by Oace.

XQ. But it was not to prove that there was not any of the single unit propylene adipate in it. Is that what you now say? A. It was not to prove that because that I knew already by looking at the acid number.

[618] XQ. You can tell that by looking at the acid number although Dr. Beavers cannot? A. You can compute it. Nobody asked Dr. Beavers about that.

XQ. They asked him whether there was any monomer material in there, and he said he couldn't tell? A. Look at the acid number and you can compute it. Your men can compute that there can't be solitary building blocks in there. That's the ordinary art of alkyd manufacture. When you get the acid number down, the reactants have combined in.

. . . . . .

[625] A. Perhaps I should correct myself. We made the tests on other tape samples earlier by the same method, and we tested samples which were plasticized with G-25 alone, G-40 alone, and a mixture of G-25 and DOP, and a mixture of G-40 and DOP.

. . . . . .

XQ. How did the weight loss compare with the weight loss of the ethyl acrylate sample? A. The weight loss of the G-25 and G-40 samples, as I recall, was under one-tenth of a per cent in the first day. We did not measure in the first

day the weight loss on the mixed DOP samples, but after ten days the weight loss on the resin-plasticized samples was of the order of magnitude of one-half per cent, and the weight loss after ten days of the DOP samples was of the order of five per cent in this test, on a rather constant slope curve, from which we could interpolate that the loss in one day might have been of the order of one-half per cent. So, as nearly as we could tell from our tests, the loss of these three types after one day would be one-tenth per cent on the resin-plasticized [626] samples, perhaps half a per cent on the tapes made according to Oace, and three per cent on the T-14 sample.

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[627] XQ. How many patent cases have you participated in? A. This is the second.

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Redirect Examination.

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[672] Q. On page 596, the first question, have you any comment to make on that and your answer, as reported? A. I evidently missed in the question the remark "which would be somewhat comparable in physical properties to these [673] G-25 DOP mixes we are speaking of." I do not believe, generally speaking, that the conventional ethyl acrylate polymers are somewhat comparable in physical properties to these G-25-DOP mixes we are speaking of.

Q. Are what you have termed conventional alkyd polyesters compatible with polyvinyl chloride? A. No.

. . . . . .

[674] Q. Do you think that migration of plasticizer from the backing into the adhesive would cause, or could cause, loss of tack of the adhesive? A. No. I think it would not cause loss of tack, but, on the contrary, would cause greater

adhesion or even the pasty condition which has been described.

Q. What reason might there be for a loss of tack in the pressure-sensitive adhesive? A. I would expect that that reason would best be sought in the adhesive itself.

Q. You said in those tests of the tape you made to demonstrate loss of weight, or no loss of weight, in the tapes plasticized with such plasticizers as G-25 there was an infinitesimal loss. To what can that be attributed? A. I believe it's due to the absorbed water which many of these materials carry under ordinary atmospheric conditions.

Q. Do most materials carry adsorbed water of that character which would make them lose weight in a test of this character? A. A very small amount of weight, yes. I would expect, for example, that the glass from your eyeglasses would show such a loss.

Q. Reference has been made to the casting method of [675] producing these vinyl backings. Is that a method which does not involve the use of any heat? A. That involves, at the most, very low temperatures, because there the ingredients are put in solution in a solvent, they are floated on a belt or a wheel or a plate, and the solvent is evaporated to leave the film.

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WALTER M. BIERINGER, witness on behalf of defendant, Vice-President and General Sales Manager of Plymouth Rubber Company:

Direct Examination.

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[681] Q. Now you at some time heard of a plastic tape made by Minnesota Mining Company, did you not? A. Yes, indeed.

Q. And about when was that? A. Oh, I imagine from its inception almost; when they started to merchandising to the electrical wholesalers, whenever that was. I would imagine around 1947, maybe 1948, I don't know, around probably 1947, they sent out circulars to all the electrical wholesalers and put on many missionary men, so I was bound to know it right at the start.

. . . . . .

Q. Do you remember what your initial reaction was about that tape? A. Well, my feeling at the very beginning was that it [682] wouldn't go over, that it was far too expensive as compared to friction and rubber tape.

Q. Well, what were the price ranges, in general? A. As I recall it, their material sold to wholesalers in large quantities, I have forgotten exactly, somewhere between 93 and 98 cents a roll for a 63-foot roll; I think I am in the approximate range there, and friction tape was selling at about 22 or 23 cents, and rubber tape, I will say, twenty-something, 25 or 26 cents, so that it was very much more expensive, and for that reason I didn't think that it was going to be successful.

. . . . . .

[683] Q. Now did there come a time when you had a more active interest in plastic tape and in making it yourself? A. Yes.

Q. And about when did that active interest arise and what was the occasion of it? A. Well, after Van Cleef Brothers began manufacturing it I became interested, because Van Cleef Brothers were competitors of ours on friction and rubber tape, which Minnesota was not, and I felt that we couldn't afford to let Van Cleef get in to our customers with this tape, no matter how small the quantities might be, because they might then also get in on the

friction and rubber tape, and it was from that time on that I became interested.

Q. Had you at that time become aware that Minnesota was making quite a go with it? A. I had no way of knowing what their volume was, but I knew they had a fair distribution all right, because many of our customers had it in stock.

[684] Q. Do you remember when it was—I think it's been testified in this case by plaintiff—that Van Cleef came out with theirs? In the last of 1949—does that conform to your recollection? A. I think it was in 1949; I'm pretty sure that was the year.

Q. Well, what did you then do about it? A. Then I got in touch with our factory people and told them I was interested in having them manufacture this product. By that time I had samples to give them, and was informed that they had already done some work on it.

. . . . . .

[685] Q. Now, when you decided to go into this project commercially, did you do anything about the matter of patents? A. Yes. I had seen patent numbers on—I have forgotten whether it was on Minnesota Mining's cartons or on circulars, but I had seen patent numbers, and I asked Mr. Danovitch, in our laboratory, to check on those numbers and see whether or not there was any conflict or any infringement.

Q. Well, did he do so? A. Yes.

Q. And did you instruct him to go to counsel, to take it up with them? A. Yes.

Q. And what was the result? A. Well, I subsequently learned that the counsel had reported that we had not infringed on any of the numbers that were checked.

Q. Did Mr. Danovitch give you the report rendered by counsel? A. Yes, he did.

Q. Is this the report that was given to you by Mr. Danovitch? A. Yes.

. . . . . .

[693] Mr. Kinney: The witness has testified about what Mr. Danovitch told him that the attorneys said.

The Court: Well, I will exclude that part of it.

Mr. Kinney: That is hearsay.

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A. Excuse me, I didn't finish that last answer entirely. In addition to what is evidently being excluded, I also telephoned long distance to Van Cleef Brothers to ask them if they knew of any patents, and they said—

. . . . . .

A. They said in their opinion there was nothing to worry about on the patent angle.

. . . . . .

[694] Q. (By Mr. Holmes) When did you first hear that a patent had issued to Minnesota Mining which had to do with this plastic tape, Mr. Bieringer? A. I believe it was in 1951, the fall, I believe, of 1951. It may have been in September or October of that year.

Q. And what was the occasion? A. I was asked by the Boston office of Minnesota Mining whether or not I could see two of their officials if they came to Boston, and it was on that occasion I had lunch there with their Mr. Halpin, I believe it was, their Vice-President, and Mr. Westbee. We had lunch at the Ritz Carlton Hotel, and during that luncheon Mr. Halpin pulled this patent out of his pocket and asked me if I had seen it. I said that I had not, knew nothing about it, and that was the first time that I had any introduction to it.

Q. Have you identified that as what we have termed the original Oace patent in suit? [695] A. Yes, that's correct.

Q. Did Mr. Halpin make any observations about the patent? A. Yes. He said he didn't know if it had any value or not, but if they should decide that it had value at a later date, would I be perhaps interested in sitting down with them and discussing some license arrangement.

Q. What was your comment on that? A. I told them if it were to the advantage of our company we certainly would discuss it.

Q. Did Mr. Halpin make any charge or suggestion that you were infringing this patent? A. No.

Q. Now this suit was brought in August, 1954—is that correct?

. . . . . .

Q. Now between that time, when you met Mr. Halpin at the Ritz Carlton Hotel, that you have just referred to, and August, 1954, when this suit was brought, did you have any other meetings with representatives of the Minnesota Mining Company? A. Yes, on two occasions I remember during electrical conventions receiving telephone calls from either Mr. Westbee or Mr. Halpin. I don't remember which one telephoned me, [696] but they wanted to see me. On one occasion I believe it was in Atlantic City; the other one I am positive was in Chicago. Then on a third occasion they asked to see me and came to my office at our factory in Canton, Massachusetts.

The Court: About what date was that that they came to see you?

The Witness: It was all prior to the bringing of the lawsuit. I don't remember whether it was 1952 or 1953.

Q. (By Mr. Holmes) Did you speak of meeting them at the electrical convention at Atlantic City? A. Yes.

Q. And the occasion of their coming to Canton? A. And in Chicago.

Q. And what, in general, were the subject-matters discussed at those conferences? A. Well, their chief interest was that we should get our prices up, particularly in one instance they wanted us to raise our prices to meet theirs in the case of a very large public utility—

. . . . . .

[697] Q. (By Mr. Holmes) Was any further mention made of this patent to which you referred at any of these later meetings with representatives of the Minnesota Mining? A. No, at no time.

Q. Did they, or any of them, ever charge you with infringement of the patent? A. No, sir.

Q. That is, until suit was filed? A. Yes. Prior to the suit, no mention was made of it.

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Redirect Examination.

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[702] Q. I neglected to ask you, Mr. Bieringer, when you were handed at the Ritz, at that first conference, when you were handed the patent in suit, the original patent, what did you do with it? A. I took it down to the factory the next day when I went out there and handed it to Mr. Hamilburg, our President.

Q. Do you know what he did with it? A. Yes, he sent it to our regular attorneys.

. . . . . .

FRANK L. KOZOL, witness on behalf of defendants, of Friedman, Atherton, Sisson & Kozol, General Counsel of Plymouth Rubber Company:

Direct Examination.

. . . . . .

[703] Q. Did you at some time, consider and take up the matter of insurance, patent insurance, and will you tell us the circumstances and when you did that? [704] A. I did take up such a subject matter sir. It was in the very late summer or in the early part of September, 1950, and it occurred in my office.

Q. Well, what was the occasion of your doing that? A. The President of the Plymouth Rubber Company, Mr. Joseph M. Hamilburg, came to visit with me by appointment, and on that occasion he directed some inquiries to me. We had a conference and a long discussion. On that occasion he told me that the company was about to embark on the manufacture of a plastic tape which had been developed by the company's chemical department, that the Minnesota Mining and Manufacturing Company had manufactured a plastic tape and that it had been brought to his attention somewhere a patent number or numbers were indicated, and that he had requested an opinion from patent counsel for the company, namely, Fish, Richardson and Neave, that he had that opinion with him, and he displayed it to me. I read the opinion. I then said to him: "I would not want any better opinion, because you know as I've told you—

. . . . . .

[705] A. I told him I would not want any better opinion. I reminded him that some years before when I first sent the company to Fish, Richardson and Neave, that I characterized them as one of the great leading patent firms of this country, that I had implicit confidence in their stature and ability, I was perfectly content to be guided in this field by their judgment. He then said to me—

Mr. Holmes:

Q. The opinion, I take it, that you were not infringing? A. The opinion was that indeed. He then said to me that he did not want to have any difficulty and if there were any questions whatsoever, he would just simply refrain from having his company go into such a situation like that because the Minnesota Mining people had a reputation throughout the country to be quick to sue, that they employed tactics of harrassment—

. . . . . .

[707] A. Well, I then asked him whether he was intent upon going forward with the manufacture of this product, being assured by the opinion of Fish, Richardson and Neave that there was no infringement with the Minnesota Mining, and he said he was, he was a little disturbed lest the Minnesota people sue some of his customers. I told him that if he was prepared to rely upon the opinion of Fish, Richardson and Neave as I was, and I so advised him, to go forward and to manufacture his product, and I said to him: "I would suggest also, as a matter of abundant precaution, that you check into the cost of patent liability insurance." He asked me to do that for him and to report to him, which I did.

. . . . . .

[709] Q. And did you find that for a very small amount you could be insured against liability for yourself and customers? A. That is right.

Q. In damages? A. That's right.

Q. And did you thereafter, through my firm, make a very [710] extensive search to see if there were any patents you might possibly be infringing? A. I made that request and received a reply.

Q. Was that a search that cost several hundred dollars? A. Yes sir.

The Court:

Q. What date did you get your reply? Do you have your correspondence? A. I don't have that sir.

Mr. Holmes: I have the letter that our firm states we studied some seventy-three patents.

The Court: I was merely trying to fix the date. He said he had a report from you.

A. Some month after August but I don't recall the month.

Mr. Holmes: February 20, 1951.

Mr. Holmes:

Q. And you were advised that no other patents had been found that you were infringing? A. That is correct sir.

Q. When the Minnesota patent came out, at some time after the Minnesota patent came out, was that patent referred to you by Mr. Hamilburg? A. In the midsummer of 1951 there was referred to me.

Q. Might it not have been the Fall, because the opinion we have is in October. [711] A. Well, my recollection is upon my return from my vacation that year, which I think was in late August or early September, I don't recall exactly, but it was in that period of time.

Q. If I told you that our opinion as to that was rendered on November 6, 1951, would that refresh your recollection as to when this patent was called to your attention? A. Well, obviously it was sometime prior to that.

Q. Well, would it be very shortly prior to that? A. I should think so, sir.

. . . . . .

Q. Were you advised that you were not infringing? A. I was.

Q. Now, did you at some time—the patent in suit came out in July 1951—did you at some time discontinue the insurance? A. Yes sir.

. . . . . .

[712] Q. And what was the date? A. October, 1953. The specific date I don't know.

Q. Did you write the company that you were discontinuing and "no claims of any type are anticipated"? A. I wrote that sir.

Q. What was the occasion of your discontinuing even this small insurance payment? A. That followed and was consonant upon a conference I had with the President of the Plymouth Rubber Company, and on that occasion I discussed the insurance situation with him. I indicated my judgment, that even though the inusrance premiums were not large, not excessive, I didn't think it made much sense to continue it because if there was any concept of possible infringement, surely we would have heard from the Minnesota Mining people before now, and under those circumstances I thought it no sense to spend any further money on insurance premiums, and advised that it be discontinued, and the President of the company accepted my advice.

Q. And in that conference did you have in mind that you had been advised you were not infringing? A. I discussed that with Mr. Hamilburg and predicated part of my judgment on that advice.

. . . . . .

Cross-Examination.

. . . . . .

[714] XQ. Well how could you happen to recommend that they take insurance? A. Well, I said to Mr. Hamilburg, that nobody could be so all-wise or all-knowing even with the ablest legal opinion obtainable, and that it might make sense out of an abundance of precaution, to get insurance if it didn't cost too much, just as I insure my house for full

value although it can't be burned down because it's brick and tile.

. . . . . .

[715] XQ. Well, it was just on an off chance that there might have been an infringement. There wasn't any question of an infringement of the patent in suit at that time, definitely? A. Of course not. The patent in suit wasn't existent then.

XQ. Now was there a search made beyond the search that was made by Fish, Richardson and Neave with respect to these patents that were existing before the patent in suit issued? A. There was another search made by another patent firm.

XQ. When? A. When I came to arrange for the insurance.

XQ. You mean there was an independent search made that you had to provide in order to get this insurance? A. There was an independent search made, yes sir.

. . . . . .

[716] XQ. The second report we're talking about? A. Oh. They too made what they represented to be an exhaustive search, in such manner as patent lawyers do it, and reported to me their complete satisfaction that there was no infringement between Plymouth's product and anything covered by the patents that they had found.

XQ. Rather broad wasn't it? A. Yes.

XQ. Who was that firm? A. Kenway, Witter—it's a long name. Kenway, Witter is the way we refer to it in Boston, an eminent patent firm.

. . . . . .

Excerpts from Deposition of Morris M. Danovitch, Taken by Plaintiff at Boston, Massachusetts, February 9-16, 1955.

Deposition of MORRIS M. DANOVITCH, witness for plaintiff, chemist, in employ of Plymouth Rubber Company, since July, 1924:

Direct Examination.

. . . . . .

[13] Q68. I think you said, Mr. Danovitch, that you commenced on this development in the year 1948. Do you remember whether that was early in 1948 or late in '48? A. No. It was late '48.

. . . . . .

Q77. Well now, what did you use as a guide when you started [14] in '48 on that tape? A. What did I use as a guide?

Q78. Yes. Anything? A. Oh, just the knowledge that I acquired from my experience on my work with plastics in other lines, and also in peroxyllins. I at one time handled all our peroxyllin coating materials, so I was familiar with plasticizers and resins, and I had a pretty general knowledge of the trade at the time.

. . . . . .

[23] Q144. Well now, when you started working on this project of making this pressure-sensitive, stretchy, retractable, [24] vinyl chloride insulating tape, didn't you at least have the "Scotch" electrical tape of commerce to guide you? A. We had some "Scotch" tape but not to guide us. Just to look at.

. . . . . .

[29] Q194. Do you know anything about the chemical nature of Paraplex G-40 by word of mouth or otherwise? A.

No, not too much chemically. I only know what it will do and what it does.

. . . . . .

[32] Q214. Were those two different ingredients a polyester type material and a liquid material? A. In some cases.

Q215. And in some cases was one of the ingredients Paraplex G-25 and the liquid ingredient dioctyl phthalate? A. Yes. But in every case the amount of liquid plasticizers was a very small minute part.

. . . . . .

[39] Q252. We are not talking about your commercial product at the moment. Some of these sample rolls that you made up in the laboratory in the 1948 to 1950 period when put in the oven for the 24-hour aging test at 100 degrees C., some of them went gooey? A. That is right.

Q253. Now did you have any understanding of why they went gooey? A. Yes.

Q254. What was your explanation of that? A. It was due to the liquid plasticizer.

Q255. And due to it doing what to what? A. Migrating, coming out from the plasticizer into the rubber. Coming out from the plastic film into the rubber adhesive. In other words, I found that DOP would do that and tricresyl would.

Q256. Did you find they would do that even if present only in small proportions? A. Yes.

. . . . . .

[41] Q269. The pressure-sensitive adhesives then that are used commercially are bought by Plymouth Rubber? A. That is correct.

Q270. And does your supplier give you the formulation of those adhesives? A. No, sir. I don't know what he uses.

. . . . . .

[51] Q345. About what proportion of your time during that two-year period would you estimate was devoted to this plastic tape project? A. Not too much.

Q346. 5%? A. Maybe 5 or 10%.

. . . . . .

[254] Q829. Did you have any analysis made of the Minnesota Mining tape then on the market? A. No.

Q830. Did you make an analysis of it? A. No. We had no way of making any analysis in our laboratory. We haven't the equipment.

Q831. Did you or your company have the product analyzed on the outside then? A. No, sir.

Q832. Did you at that time know that the "Scotch" Brand No. 33 electrical tape was made with a polyvinyl chloride [255] backing? A. Yes.

Q833. Did you know that the backing contained a plasticizer material? A. Yes. Couldn't make any vinyl. That is just natural.

Q834. Did you know what the plasticizer material was at that time? A. No, sir.

Q835. Did you sometime later learn what it was? A. No. Only until after the patent came out.

Q836. Which patent? A. Your first one there.

. . . . . .

[383] Q1369. Now did that tape turn out all right? A. No, that did not.

Q1370. What difficulty did you have with that? A. We got migration due to pastiness of adhesive.

Q1371. Your adhesive became pasty? A. Yes. Which I attribute to the addition of the DOP.

Q1372. Do you have any test data that shows that? A. No, because anything that was bad I didn't ordinarily keep. I had no interest in it.

Q1373. No test data to show that? A. No.

Q1374. You know very well that Minnesota Mining's production for years had DOP in it as well as a polyester plasticizer and was perfectly satisfactory tape, don't you? A. Well, so it said in the patent that came out in late '51.

Q1375. You made formulations up according to that patent, didn't you? A. I did not.

Q1376. You have never done that? A. I did not. In fact, in my early work that patent wasn't even out.

. . . . . .

[386] Q1398. Yes. Read it all in. A. "T-345. 33 in a circle. Mixed 2/29/52. 7 minutes high, 8 minutes low. Temperature 325 degrees. Looks softer than regular and not so dry. Stuck to mill in mill room." I don't know what that last figure is. "Added one pound calcium stearate and was better. Send out to No. 5. Stuck to feed mill and then when started to calender had all kinds of trouble. Calender at time 340 degrees F. Took two hours to get going again second time. Have had trouble with G-25. Top side was smooth. Under side rough rough as hell. Something rotten in Denmark." I recall this particular one. I had a lot of trouble with it.

. . . . . .

[416] Q1587. Now do you know why this G-25, when used alone or in high proportion or without the presence of DOP, caused [417] some difficulty in calendering?

Mr. KIRKPATRICK. Are you still talking about that period of that document, February 6, 1952?

Mr. KINNEY. Yes. That time or earlier.

A. No, I don't. We never were able to calender G-25 successfully as a film.

Mr. KIRKPATRICK. In that period?

The WITNESS. During that period. As my own records show.

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Cross-Examination.

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[535] XQ2161. Then, as I understand it, those liquid plasticizers, dioctyl phthalate, tricresyl phosphate or whatnot, tended to make easier the mixing or dispersal in the resin, but you were not able to use them in your adhesive tape work because of migration troubles with the adhesive on the plastic tape? A. Yes. My work showed that wherever I used these liquid plasticizers I got migration of the plasticizer.

. . . . . .

[556] XQ2239. Is it true, Mr. Danovitch, that it was always difficult and still is difficult to some extent at least to run [557] your regular G-40 tape material? It requires some machine tricks and the like? A. Yes, to a certain extent.

XQ2240. And in that respect has it been your experience that G-25 has been still harder to run, at least up to May of 1954? A. Yes. My experience prior to that was we were never able to run G-25.

XQ2241. Now what enabled you to run that G-25 successfully? I hand you Exhibit 18 for identification in this connection [indicating]. A. The only reason we could run this was we found a lubricant which helped us to get this off the calender.

XQ2242. Would you have been able to run it without that lubricant? A. No.

XQ2243. That particular lubricant you have indicated is this 407 wax appearing on Exhibit 18 for identification? A. Yes.

. . . . . .

[558] XQ2244. Had you always had trouble with G-25 prior to the time of incorporating 407 wax therewith? A. Yes.

XQ2245. Were you able to run anything satisfactorily with G-25 alone? A. No, we were never able to.

XQ2246. And that was true up until May of 1954? A. Yes.

XQ2247. Now what was the reason for developing this formula, Exhibit 18 for identification, incorporating the wax and the G-25, the G-25 being the sole plasticizer? A. That was for the purpose of meeting new government specifications on plastic tape that was out.

XQ2248. And would your G-40 tape meet that new Government specification? A. No. There were certain requirements in the specification where our regular production would not meet it.

. . . . . .

Redirect Examination.

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[580] Q2353. Who suggested the use of that wax? A. My best recollection is it came from a salesman.

. . . . . .

[590] Q2396. Now I understood you to say, in answer to your counsel's questions, that you found that liquid plasticizers tended to make the adhesives go pasty? A. That is correct.

Q2397. You were referring to the liquid plasticizers when used as the sole plasticizer for the vinyl resin, is that right? A. No. I was referring to when it is used in combination.

Q2398. Well, was it your intention to generalize and say that a liquid plasticizer, when used in combination with other plasticizers, will nonetheless make the adhesive coating pasty? A. That has been my experience right along.

. . . . . .

Recross-Examination.

. . . . . .

[600] XQ2448. As a final question, is it correct to say that a given batch of any given formulation could succeed or fail in actual commercial production depending on how it is handled by the, we will say, Banbury and the milling and the calender people? A. Yes.

. . . . . .

Excerpts from Plaintiff's Exhibit 2—File History of the Original Oace et al. Patent in Suit No. 2,559,990.

Original Claim 3

[Ex. 2, p. 17:]

"3. A stretchable and elastic pressure-sensitive adhesive tape adapted for use as an electrical insulating tape for wrapping wire and cable splices, comprising a film backing compounded of a vinyl chloride polymer blended with a low molecular weight liquid plasticizer in amount not exceeding about 20 parts per 100 parts of the vinyl chloride polymer and a non-migrating high molecular weight plasticizer imparting additional elasticity, and a water-insoluble and non-corrosive normally tacky and pressure-sensitive adhesive coating firmly united to the film backing, the adhesive coating and backing film being in permanent equilibrium so that the adhesive is stably tacky and eucohesive, and the adhesive tape being stretchable to the extent of at least about 50% at room temperature and being substantially completely retractable from an elongation of 30%."

Excerpt from Patent Office Action of March 4, 1947.

[Ex. 2, pp. 22-23:]

"Claims 3, 6, 7 and 8 are rejected as involving no invention over Morgan or Eustis in view of Robertson and Groff. The primary references teach that a vinyl resin film may be employed as a backing for a pressure sensitive adhesive base. Obviously to modify such base with plasticizers, pigments, stabilizers or the like would involve nothing patentable, especially since the secondary references

show that vinyl resin films may have different physical characteristics dependent on the modifying agents included in the film.

"Claims 3, 6, 7 and 8 are further rejected as failing to properly define the invention as required by R.S. 4888. The term 'vinyl chloride polymer' is too broad since it includes all polymerized resins which may include some vinyl chloride. The disclosure does not warrant such broad protection. The description of the plasticizers as being 'a low molecular weight liquid plasticizer' and 'a non-migrating high molecular weight plasticizer' fails to define what these plasticizers are but relies simply on the single detail of having low or high molecular weights. This limitation is valueless in defining the actual substances employed. The statement that the adhesive is in permanent equilibrium with the film backing sets forth nothing more than a desired result since it fails to include sufficient details to show how this permanency is obtained."

Excerpt from Patent Office Action of May 11, 1948.

[Ex. 2, p. 33:]

"Claims 3, 4 and 6-9 are rejected as unpatentable over Morgan or Eustis in view of Robertson and Groff for reasons set forth against claims 3, 6, 7 and 8 in Paper #2a. The claims of this application set forth an adhesive tape having desired characteristics which are imparted thereto primarily by the use of plasticizers which are old for plasticizing vinyl resin films. No invention is seen in applying an adhesive coating to a vinyl resin film which is modified in accordance with the teachings of the prior art. Although applicants argue that they have attained commercial success with their product, it is not seen that this argument

is convincing since the claims do not define patentable subject matter. See In re Normann et al, 150 Fed. (2nd) 708; 66 U.S.P.Q. 308."

EXCERPT FROM AMENDMENT OF NOVEMBER 8, 1948.

[Ex. 2, pp. 34-35:]

"Please cancel claims 1 to 9, inclusive (all of the present claims) and add the following claims:

"1. A pressure-sensitive adhesive insulating tape wound upon itself in roll form and comprised of: a stretchable and elastic film backing having a thickness of 4 to 20 mils and formed of a homogeneous mixture primarily consisting of a stable blend of a film-forming polymer of monomers including at least a major proportion of vinyl chloride, a substantially non-volatile liquid phthalyl ester plasticizer amounting to 8 to 20 parts per 100 parts of said polymer, and a soft and viscous low-acid-number alkyd plasticizer resin in amount at least equal to the amount of said liquid phthalyl ester plasticizer, the total amount of said plasticizers being about ⅓ to ½ the amount of said polymer and the proportions being such that the adhesive tape has the properties of stretch and elasticity hereafter specified without causing pastiness or tack-loss of the contacting adhesive in the roll; and a eucohesive normally tacky and pressure-sensitive rubber-resin type adhesive coating united to the inner face of said film backing; said adhesive tape being unwindable without delamination or offsetting of adhesive, being originally stretchable by hand-pulling to an extent of at least 50% at room temperature and being substantially completely retractable from an elongation of 30% as herein specified."

[This claim as amended became claim 1 of the issued patent.]

EXCERPT FROM APPLICANTS' REMARKS, ACCOMPANYING AMENDMENT OF NOVEMBER 8, 1948.

[Ex. 2, p. 41:]

"The *Robertson* patent relates to an alleged novel technique for making vinyl resin films. Beginning with line 63, col. 2, page 2, reference is made to plasticizers. These plasticizers may be used 'in any amount up to about 20% or somewhat more based on the weight of the vinyl resin'. There is no suggestion of the three-way blend used by applicants, employing the vinyl chloride polymer, the liquid phthalyl ester, and the alkyd resin, *combined together*. That this three-way blend is essential to the success of applicants' product was clearly pointed out in the application as filed. Thus on page 2 it was pointed out that the phthalate plasticizer used alone resulted in inadequate stretch and elasticity, particularly in respect to backings of the thickness used in electrical tapes. If the plasticizer proportion is increased, the film becomes unsuitable because it makes the adhesive become soft and pasty. On the other hand, the resinous type plasticizer, if used alone in sufficient amount to impart desirable physical properties, results in the adhesive losing its tack (top of page 5). Obviously this Robertson patent does not teach applicants' discovery—first because it does not disclose their backing film, and second because it teaches nothing about the problems of pressure-sensitive tape backings."

EXCERPT FROM APPLICANTS' REMARKS ACCOMPANYING AMENDMENT OF NOVEMBER 4, 1949.

[Ex. 2, p. 54:]

"As was pointed out in the interview, claims 10 and 12, together with dependent claims 11 and 13, are clear and definite with the amendments here presented. Soft and

viscous alkyd resin is shown in the specification to serve as a plasticizer for the vinyl chloride polymer, and adds properties thereto which are not made available by a mere increase in the proportion of liquid phthalyl ester plasticizer. (The reverse is also true, as is apparent from the specification.)"

EXCERPT FROM PATENT OFFICE ACTION OF MAY 24, 1950.

[Ex. 2, p. 56:]

"Claims 10-13 are further rejected as too broad as to the description of the base material. It is obvious that the particular type of vinyl resin used in combination with controlled amounts of specific plasticizers are factors which go to the essence of the alleged invention and should, therefore, be specifically defined in the claims. Applicants have indicated in their specification that specific plasticizers are required to produce their insulating tape having certain desired properties of elasticity. The use, therefore, of the broad expressions 'a liquid phthalyl ester' and 'a soft and viscous alkyd resin' are objected to as unduly broad."

EXCERPT FROM APPLICANTS' REMARKS ACCOMPANYING AMENDMENT OF OCTOBER 12, 1950.

[Ex. 2, p. 60:]

"Additionally, it should be noted that the claims require the tape backing to be formed of a *homogeneous* mixture of a *stable blend* of the components having *stated proportions.* These requirements, together with the stated requirements as to the individual components, effectively and adequately define the tape product in terms which fully distinguish over the prior art."

Excerpts from Plaintiff's Exhibit 4, File History and Contents of Reissue Patent in Suit, Re. No. 23843.

ORIGINAL CLAIM 7.

[P. 15:]

"7. As a new article of manufacture a pressure-sensitive adhesive insulating tape comprising a high di-electric strength, water-insoluble and hydrocarbon oil insoluble backing film from 4 to 20 mils thick comprising a stable film-forming blend of polymer material and plasticizing material therefor sufficient to produce a film which in the above thicknesses is stretchable by hand pulling to an extent of at least 50% at room temperature and substantially completely retractable from an elongation of at least 30%, and a water-insoluble pressure-sensitive adhesive coating on one side of said backing film, the plasticizing material of the backing film being selected with respect to the polymer material thereof and with respect to said pressure-sensitive adhesive so as to avoid causing said adhesive to become pasty or to lose its tackiness upon prolonged and intimate contact thereof with said backing film, said insulating tape being capable of being formed into rolls or stacks of superimposed, contiguous layers thereof and subsequently removed therefrom without damage to the backing or offsetting of the adhesive."

EXCERPT FROM INVENTORS' OATH ACCOMPANYING REISSUE APPLICATION.

[Pp. 22-23:]

"Deponents failed adequately to explain to their attorneys the nature and characteristics of the materials described in the specification, and the relationship of the characteristics of said materials to each other, from which

the actual scope of the invention may be determined, and the importance of the details thereof. Each and all of the Deponents were virtually without any prior experience in connection with patents at the time of their original application. In interviews had within the last month, it became apparent to Deponents that their invention was not sufficiently or adequately claimed, within the scope of the inherent qualities of the illustrative embodiments of their invention, and that the claims of their original patent therefore were not sufficient to adequately cover their invention. In particular, it became apparent that Deponents themselves, upon a reading of the specification, could readily suggest how to evade the scope of each of the claims, while making the product defined in their patent."

EXCERPT FROM PATENT OFFICE ACTION OF AUGUST 7, 1952.

[P. 27, par. 6, 1st sentence:]

Claims 6 to 14 inclusive are rejected as being too broad and indefinite, and as failing to comply with Section 4888 of Revised Statutes. The expressions "film-forming blend of polymer material" (claims 6, 7, 13, 14), or backing "having the vinyl linkage" (claim 8) do not specify any particular type of materials; the application discloses only certain particular copolymers of vinyl chloride.

AMENDMENT OF MAY 12, 1953—ADDITION OF NEW CLAIM 16, WITH AMENDMENTS. (THIS CLAIM BECAME CLAIM 6 OF THE REISSUE PATENT.)

[Ex. 14, p. 58:]

6. A pressure-sensitive adhesive insulating tape wound upon itself in roll form and comprising: (1) a water-insoluble and hydrocarbon-oil-insoluble film backing of high

dielectric strength containing a stabilizer and having a thickness of 4 to 20 mils and formed of a homogeneous mixture primarily consisting of a stable blend of (a) a film-forming polymer of monomers including at least a major proportion of vinyl chloride, and (b) a substantially non-volatile plasticizing material therefor in an amount within the range of at least ⅓ the weight of said polymer but in a substantially lesser amount than said polymer and comprising at least a major proportion of a non-migrating viscous plasticizer resin, and the proportions being such that the adhesive tape has the properties of stretch, elasticity and retractability hereafter specified without causing pastiness or loss of the tack of the contacting adhesive in the roll; (2) an adhesive primer coating on the inner face of the film backing adapted to increase the anchorage of the adhesive coating; and (3) a water-insoluble normally tacky and pressure-sensitive rubber-resin type adhesive coating united to the inner face of said film backing, over said primer coating, said adhesive coating being thin in relation to said film backing; said film backing being in permanent equilibrium with said pressure-sensitive adhesive coating so as to avoid pastiness or loss of tack of the said adhesive coating and diminution of the flexibility of said film backing; said adhesive tape being unwindable from the roll without delamination of the tape or offsetting of the adhesive, being originally stretchable in widths not greater than about one inch by simple hand pulling, exercising a force of not more than about 10 to 15 pounds, to an extent of at least 50% at room temperature and being substantially completely retractable from an elongation of 30%, as herein specified; said tape being readily conformable to irregular surfaces in insulating wire splices and its elasticity, retractability and high adhesion value making it easy, in insulated splices, to produce snug wrappings and coverings, and said tape having sufficiently aggressive ad-

Defendant Ex 12 4

Period Ending
May 15, 1944

TO: DR. H. N. STEPHENS

Research Department
Adhesive Section

SEMI-MONTHLY REPORT

* * * * * * * * * * * (Page 4)

AR42 - Elastic Plasticisers - Dr. W. E. Lundquist and Esther Eastwold

Work is under way in the evaluation of polyvinyl chloride films which have been plasticised with a number of commercially available plasticisers. First evaluation of interest is that which concerns the possible migration of plasticiser to the adhesive. Tests were started in which samples of each acrylate, alkyd, and rubber cellophane tape were placed in contact with the plasticised

(Page 5)

films for the purpose of determining adhesion and effects on the adhesive after stated intervals of time. In the majority of the cases the adhesion was so high that the adhesive either stripped from the backing or the film-tape combination could not be held down to the glass plate with double coated tape. Consequently, the films have been coated with each the rubber adhesive and the acrylate adhesive and the adhesion tests will be made from strips cut from these coated films. Observations will also be made for the development of stringiness in the adhesive.

/s/ J. O. Hendricks 5-23-44
Adhesive Research Laboratory

Period Ending
July 15, 1944

TO: DR. H. M. STEPHENS

Research Department
Adhesive Section

SEMI-MONTHLY REPORT

* * * * * * * * * * * (Page 3)

AR42 - Elastic Plasticisers - Dr. W. E. Lundquist and Esther Eastwold

One group of tests of different adhesives coated on various plasticised polyvinyl chloride films is nearing completion. The alkyd and Vistanex adhesives appear undesirable in that the

(Page 4)

former has too low adhesion and the latter becomes pasty and stringy. Better results have been obtained with bakelised acrylate, natural rubber, and GR-S base adhesives. From the tests of adhesive strips against their own backings, Paraplex G25 as a plasticiser has shown up well. The strips were held at 120 and 150°F. for a period of one week. The plasticizer may affect the adhesive, but rather than causing the latter to go pasty, it becomes drier and has less tack.

* * * * * * * * * * *

/s/ J. O. Hendricks 7-21-44
Adhesive Research Laboratory

Period Ending
July 31, 1944

TO: DR. H. M. STEPHENS

Research Department
Adhesive Section

SEMI-MONTHLY REPORT

* * * * * * * * * * (Page 4)

AR42 - Elastic Plasticisers - Dr. W. E. Lundquist and Esther Eastwold

The series of tests described previously have now been

(Page 5)

completed. The Vinylite VYNW (Carbide polyvinyl chloride) was plasticised with each of Paraplex G25, tricresyl phosphate and dioctyl phthalate. On each plasticised film the following adhesives were coated: Vistanex, alkyd, bakelised acrylate, Buna S and rubber. The adhesive coated films were left in contact with their own backing over a period of time at room temperature, at 120°F., and at 150°F.

The alkyd and Vistanex adhesives gave poor results with each of the plasticised films. The softening effect of the various plasticizers on the adhesives listed in decreasing order was dioctyl phthalate, tricresyl phosphate, and Paraplex G25. PG25 caused splitting of the bakelised acrylate and a reduction in adhesion of the Buna S adhesive. The rubber adhesive on the PG25 plasticised film remained in fairly good condition but there was a reduction in wet grab and the anchorage was not too good. In general, the effect of higher temperature was to speed up the phenomena occuring at a slower rate at room temperature. From the results it is seen that PG25 is the best plasticizer to use with respect to least harmful effects to the adhesive. Apparently, this plasticiser is less compatible with polyvinyl chloride than either TCP or DOP, since the tensile strength of its plasticised film was lower than either of the films plasticised by the others.

The results showed that the possibility of obtaining a mending tape having a DOP plasticised film as the backing was not very good on account of the effect of the plasticisers on the adhesive. The alkyd adhesive was least effected by this plasti-

Defendants' Exhibit 6

268 5

4-4-46

Prep of films for obtaining tensile & sketch data

30 g of solution used in each of following

1	XYNL - RB2	(80:20)	(7.5g XYNL)	1.88g RB2	
2		(82:18)		1.65g RB2	
3		(85:15)		1.33g RB2	
4	VYNS - RB2	(85:15)	6.9g VYNS	1.22g RB2	
5		80:20		1.73g RB2	
6		75:25		2.3 g RB2	
7		70:30		2.96g RB2	
				BKO	DOP
8	VYNS-BKO-DOP	(85:5:10)	6.9g VYNS	.41g	.81
9		(82:10:8)		.84g	.67
10		(80:10:10)		.87g	.87
11		(85:10:5)		.81	.41
14		80:15:5		1.13	.375
12	VYNS - BKO	(83:17)	6.9 g VYNS	1.42 g BKO	
13		(80:24)		1.73 g BKO	
15	Gen 216-DOP-BKO	(80:5:15)	6.g Gen 216	.375 g DOP	1.13g BKO
16		(84:8:8)		.57g DOP	.57g BKO
17	Gen 216-BKO	(80:20)	6g Gen 216	1.5 g BKO	
18		(77:23)		1.8 g BKO	

Cast on glass plate, dried in 65° C oven over nite
#6 & 7 are sticky - emulsion, 4,5,6,7 are somewhat opalescent & whitish.

4 VYNS - RB2 (85:15) 6.9 g VYNS 1.22 g RB2
5 80:20 1.73 g RB2
6 75:25 2.3 g RB2
7 70:30 2.96 g RB2
BKO DOP
8 VYNS-BKO-DOP (85:5:10) 6.9g VYNS .41g .81
9 (82:10:8) .84g .67
10 (80:10:10) .87g .87
11 (85:10:5) .81 .41
14 80:15:5 1.13 .375
12 VYNS - BKO (83:17) 6.9 g VYNS 1.42 g BKO
13 (80:24) 1.73 g BKO
15 Gen 216-DOP-BKO (80:5:15) 6.g Gen 216 .375 g DOP 1.13g BKO
16 (84:8:8) .57g DOP .57g BKO
17 Gen 216 - BKO (80:20) 6g Gen 216 1.5 g BKO
18 (77:23) 1.8 g BKO

Cast on glass plate, dried in 65° C oven over nite
#6 & 7 are sticky - emulsion, 4,5,6,7 are somewhat opalescent & whitish.

Prep of 25% Solution of Gen 216
1000 g Gen 216
3000 g MEK.

Carl A Dahlquist
4-4-46

Carl A Dahlquist
4/4/46

hesiveness to remain tightly and snugly wrapped around splices and wires."

EXCERPTS FROM AFFIDAVIT OF WILLIAM E. LUNDQUIST, DATED MAY 8, 1953, ACCOMPANYING AMENDMENT OF MAY 12, 1953.

[P. 68, lines 5-14:]

"Said Exhibit D tape has imprinted on the core: 'SCOTCH' Brand Electrical Tape No. 33; and on the side of the core has imprinted: 2VBA 1 1D9L 5 C2. The backing of the tape marked Exhibit D was plasticized by the use of 32 parts of Paraplex G-40 (a high molecular weight polyester type plasticizer) and 16 parts of dioctyl phthalate (a substantially non-volatile liquid plasticizer) per 100 parts of a copolymer of 95% vinyl chloride and 5% of vinyl acetate."

[P. 75, 1st complete par.:]

"In accordance with the teaching of Oace et al (for example, see the Oace et al specification, page 5, line 23 et seq.) instead of using 2 parts of 'Paraplex G-25' (high molecular weight plasticizer) to 1 part of dioctyl phthalate (liquid plasticizer), where the 'Paraplex G-25' is replaced by a somewhat lower molecular weight plasticizer, the amount of liquid plasticizer may be correspondingly reduced or modified, with equivalent results. For example, where, instead of 'Paraplex G-25,' 'Paraplex G-53' or 'Paraplex G-50' are used to plasticize the vinyl polymer (Vinylite VYNW), the dioctyl phthalate or equivalent may be reduced or eliminated, with equivalent results. Tape has been made under affiant's directions, using 'Paraplex G-50' in one instance and 'Paraplex G-53' in another instance, and affiant demonstrated, to his own satisfaction, that the proportion of the dioctyl phthalate or equivalent may be modified suggested by Oace et al, and can be reduced to zero in such event, with equivalent results."

EXCERPTS FROM PATENT OFFICE ACTION, MAY 29, 1953.

[P. 95, pars. 2 and 3:]

"2. The denial for a reissue of patent No. 2,559,990 on the ground of estoppel is repeated.

"3. Claims 4 and 16, covering the polyvinyl chloride base film coated with a primer coating, and a superposed pressure-sensitive adhesive are allowable, provided that the Board of Appeals finds that applicants are entitled to the reissue of the patent."

EXCERPT FROM AMENDMENT OF JUNE 24, 1953.

[P. 98, lines 12-20:]

"In Office action dated May 29, 1953, the Examiner stated that claims 4 and 16 are allowable, provided the Board of Appeals finds that applicants are entitled to the reissue of the patent, i.e., provided the Board of Appeals reverses the Examiner's rejection on the ground of estoppel. Arguments in that regard are presented hereinafter.

"In view of the approved wording of claim 16, applicants have written three new claims, namely, claims 17, 18 and 19, designed to replace claims 10, 6 and 8, respectively."

Excerpts from Defendants' Exhibit 7, being a Report Dated December 20, 1944, of Esther Eastwold and W. E. Lundquist, Entitled "Elastic Solid Plasticizers—Tape Backings of Plasticized Vinyl Polymer Films," for Period from February 1, 1944, to September 20, 1944.

[P. 1:]

"In the past attempts have been made to prepare tape using plasticized vinyl chloride polymer films as backings.

These tapes failed because of migration of plasticizer from the backing to the adhesive, thereby making the adhesive too soft and stringy to be useful. Attempts have been made by the Tape Department to overcome this trouble by developing an adhesive which would be unaffected by the plasticizer in the backing, but this is a difficult problem and has not led to any usable construction.

"Under this project a study of plasticized vinyl chloride polymer films as tape backings has been undertaken to determine their effect on standard pressure-sensitive adhesives. It has been thought that if a plasticizer of high enough molecular weight were used, it would have no tendency to migrate and therefore would have no effect on ordinary pressure sensitive adhesives. About this time this work was started, Resinous Products and Chemicals Company brought out their Paraplex-G-25, which is a high molecular weight plasticizer for vinyl chloride polymers. Under the present study this resin was tested to determine what might be expected of a high molecular weight plasticizer as compared to the standard low molecular weight variety."

[P. 4:]

"Dioctyl phthalate was the most effective plasticizer tested, that is, it seemed to exert the greatest solvent power for the vinyl chloride polymers and gave the most pliable films. Paraplex G-25 had the poorest solvent and plasticizing action of the materials tested."

Excerpts from Defendants' Exhibit 8, Entitled "Elastic Solid Plasticizers—Stretchable Tape Backings," being Report Prepared by Esther Eastwold and Dr. W. L. Lundquist, Dated July 7, 1945, and being Report for the Period from September 20, 1944 to June 30, 1945.

[P. 2:]

"Vinylite VYNS-Chemigum N-1 films having high strength and stretch have been prepared. The use of about 25% of Chemigum gives strong films which elongate 50-100% before breaking whereas 40% gives strong films which elongate 400%. Vinylite VYNS films plasticized with dioctyl phthalate and Paraplex G-25 have continued to cause tack loss in standard adhesives coated on them."

[P. 5:]

"The VYNS-Paraplex G-25-dioctyl phthalate films caused loss of tack with all the adhesives tested and are probably not usable with these standard adhesives."

[P. 6:]

"Two low molecular weight vinyl chlorides copolymers (VYLS and VYHH) were evaluated. Both were too weak and brittle to be of interest.

Excerpt from Defendants' Exhibit 9, Report Prepared by Esther Eastwold [Mrs. LePage] for Period August 15 to February 8, 1946, and Dated February 8, 1946.

[P. 3:]

Patent Situation

A patent application, Ser. No. 641000, Oace, Snell, & Eastwold, was filed January 12 covering Paraplex G25-Flexol DOP plasticizer vinyl chloride-vinyl acetate copol-

ymer in which not more than about 20 parts DOP per 100 parts vinyl polymer and additional non-migrating high molecular weight plasticizer, such as G25, imparting additional elasticity are used. This combination obviates the shortcomings of either when used alone; viz., loss of tack with G25 and pastiness with DOP.

Excerpts from Defendants' Exhibit 12, "Semi-Monthly Report" of Esther Eastwold (Mrs. LePage).

[P. 38:]

"Period Ending
April 15, 1946

TO: DR. H. N. STEPHENS
Research Department
Colloid Section

"Semi-Monthly Report

. . . . . .

AR 42 — Elastic Solid Plasticizers — Esther Eastwold

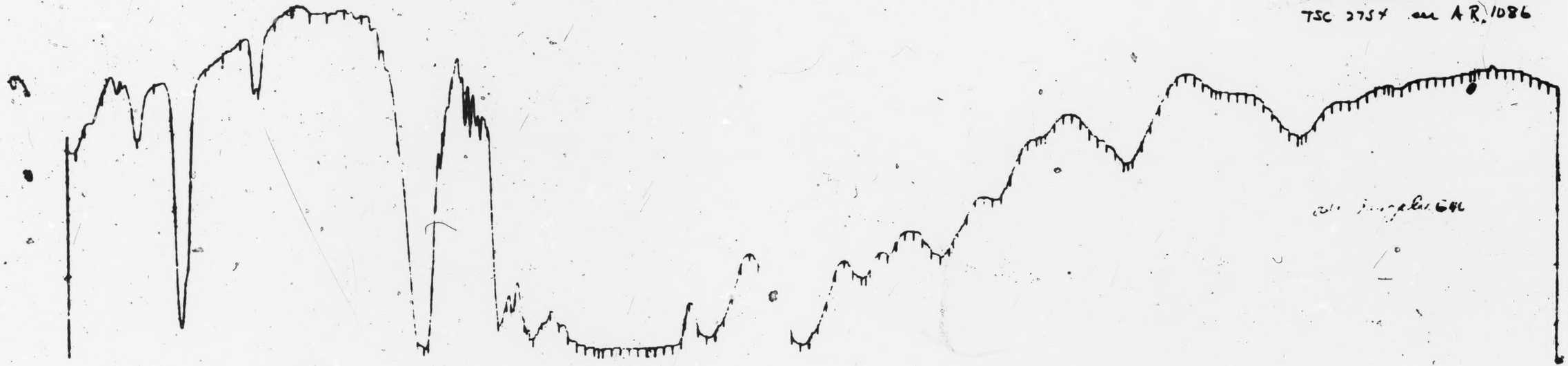
"The study of Paraplex G-40 as a plasticizer for Geon 200x5 and Vinylite VYNS has been completed, both with regard to elasticity data and to the behavior of adhesives coated on the plasticizer films. G-40 has been found equivalent to G-25. G-40 was tried as the only plasticizer and also evaluated in combination with D.O.P. Rubber adhesive A 73-5 and GR-S adhesive A 341 were considered to behave satisfactorily although there was some tack loss noted. In one formulation G-40 caused less tack loss than had been observed for G-25 in a previous evaluation. This may have been due to a lower caliper backing."

(A149)

Deft. L En 58-C ud
6/9/55 Ufs

6980. S-1957 SP
Plasticizer, Plymouth
Elect. Tape
Landolum
AMP
10270
Nat

TSC 2754 on A R 1086



Defs Exh 58 F-2

(A151)

FORM 58 5-28-50

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PERLICH
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ANALYTICAL TEST REPORT

TAPE DEPARTMENT

AP-1086

May 28, 1951

SUBJECT: Competitive Plastic Electrical Tapes.

BACKGROUND: Quantitative and qualitative analysis of the plasticizers being used by competitors in the plastic electrical tape field has been requested relative to the claims which the patent office has allowed 3M.

ANALYSIS: Extractions of 1-2 gram samples of backing, free from adhesive, were performed in Soxhlet extractors using methanol solvent. The composition of each extract was ascertained by comparative infrared absorption spectra run by Central Analytical Research over the 2 to 15 micron wavelength region

RESULTS:

Tape	% Plasticizer	Type Plasticizer
[redacted] (TSC-2806)	23.9	Polyester & phosphate
[redacted] (TSC-2809)	26.?	Polyester
[redacted] (TSC-2785)	27.9	Polyester
[redacted] (TSC-2653)	30.6	Polyester
Van Cleef Bros. Inc.		
Dutch Brand "Plastix" (TSC-2758)	35.1	Polyester
Dutch Brand "Plastix" (TSC-2720)	36.2	Polyester
Superior Insulating Tape Co.		
No. 6 Plastic Electrical	34.9	Polyester
[redacted] Tape (TSC-2828)	35.0	Polyester
[redacted] Tape (TSC-2820)	21.3	Polyester
Plymouth Rubber Co		
Plymouth Plastic Electrical Tape (TSC-2754)	24.9	Polyester
3M Co. - Control Samples		
#33 Electrical VBA (11B3N-5B4)	21.6	Polyester & phthalate
#33 Electrical 2VBA	27.9	" "
Uncoated Backing used in 2VBA above	28.0	" "
#33 Electrical VPH	23.9	" "

DISCUSSION: The increasing use of polyester type plasticizer indicates that the light, linear polyesters can give satisfactory low temperature performance while still maintaining

resistance to migration. These apparently are the salient factors in the displacement of the monomeric phthalate and phosphate plasticizers.

REFERENCE: Notebook 2141, page 1-2

R. W. Lundbohm

rwl/jh

cc-E. Bond
W. McKee (2)
L. Swanson

[redacted] 8-28-50
58-7

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(AIJS) Deft's Ex 58-Fid 6/9/55 HPB

ANALYTICAL TEST REPORT

TAPE DEPARTMENT

AP-1086

May 28, 1951

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Dutch Brand "Plastix" (TSC-2720)	36.2	Polyester
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No.60 Plastic Electrical	34.9	Polyester
[redacted] Tape (TSC-2828)	35.0	Polyester
[redacted] Tape (TSC-2820)	21.3	Polyester
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Plymouth Plastic Electrical Tape (TSC-2754)	24.9	Polyester
3M Co. - Control Samples		
#33 Electrical VBA (TSC-2754)	21.6	Polyester & phthalate
#33 Electrical 2VBA	27.9	" "
Uncoated Backing used in 2VBA above	28.3	" "
#33 Electrical VFH	21.9	" "

[redacted]

(A.E.I. v. Plaintiff)

Page 3 of Defendants' Exhibit 52, Booklet of Resinous Products & Chemical Co., "Paraplex G-25 and G-40," March 1947.

PARAPLEX

G-25 and G-40

Introduction

PARAPLEX G-25 and G-40 are resinous polyesters, permanently soft and thermoplastic in nature, and very stable. They are outstanding plasticizers for polyvinyl chloride, the vinyl copolymer resins, and elastomers of the acrylonitrile-butadiene type in applications where the ultimate in permanence is required in the finished compound.

A satisfactory plasticizer for use with polyvinyl chloride copolymers must show the basic requirements of good compatibility and efficiency, as well as satisfactory water resistance and permanence. Outstanding plasticizers, in addition, will produce a compound showing such special properities as low-temperature flexibility, oil-resistance, low flammability and heat stability. Paraplex G-25 and G-40 are unique in their ability to impart these desirable qualities to vinyl compounds. They are outstanding plasticizers for those uses where freedom from lacquer lifting is a prerequisite. They are especially valuable, therefore, in free films for handbags, luggage and similar applications.

These polyesters combine many of the desirable features of the ester-type plasticizers with the permanence and added resistance to extraction that are obtainable only in a synthetic resin plasticizer. Compounds in which Paraplex G-25 and G-40 serve as the principal plasticizer exhibit the following properties:

Resistance to oils and gasoline
Essentially zero volatility
Excellent heat stability
No plasticizer migration
Low flammability
Good low-temperature flexibility
Excellent stability on exposure to ultraviolet, particularly in the case of Paraplex G-25
Very low heat-deformation
Very good water resistance
Excellent processing properties

In this booklet has been summarized the information accumulated during extensive laboratory and field evaluation of Paraplex G-25 and G-40 since the introduction of these resinous polyesters several years ago. Additional data on specific applications will be supplied gladly upon request.

Page 6 of Defendants' Exhibit 52, Booklet of Resinous Products & Chemical Co., "Paraplex G-25 and G-40," March 1947.

COMPATIBILITY CHARACTERISTICS

Paraplex G-40 is not compatible with as wide a variety of materials as is Paraplex G-25. The compatibility characteristics of Paraplex G-40 are given in the following table.

COMPATIBLE

Polyvinyl Chloride (up to 35% G-40)
Vinyl copolymer resins (up to 40% G-40)
Buna N-type synthetic rubbers
Neoprene

INCOMPATIBLE

Cellulose Acetate (PM-3)
Cellulose Acetate (FM-6)
Polyvinyl Butyral (VF-7100)
Polyvinyl Butyral (VF-7200)
Polystyrene
Polymethyl methacrylate
Cumar P-10
Cumar P-25
Uformite F-200E
Amberol ST-137

Like Paraplex G-25, Paraplex G-40 may be handled successfully by allowing the material to stand overnight in a warm room before use. Exposure to temperatures of 88° C. for several weeks in glass containers produces little change in the color, acid number, and viscosity of Paraplex G-40. The volatility loss at temperatures up to 150° C. over a 16-hour period is negligible.

Cooling Paraplex G-40 to −79° C. in a dry ice-methanol bath causes no crystallization. Similarly, exposure for 3 days at −30° C. does not cause freezing. The material becomes hard but remains amorphous.

The wide range of conditions over which Paraplex G-40 retains its physical properties is an indication of the stability which may be expected in stocks containing this plasticizer.

When Paraplex G-40 is used with vinyl elastomers at concentrations approaching the upper limits of compatibility listed above, exposure of the material to high humidity may result in surface exudation. This must be kept in mind where Paraplex G-40 is the sole plasticizer. However, since it is common practice to use Paraplex G-40 in conjunction with a monomeric material, this problem does not arise frequently.

SECTION II—USE OF PARAPLEX G-25 AND G-40 WITH POLYVINYL CHLORIDE AND COPOLYMERS

Paraplex G-25 and G-40 have been used successfully with all of the commercially available polyvinyl chloride and vinyl copolymer resins.

MILLING TECHNIQUE

The technique used in compounding Paraplex G-25 and G-40 with the vinyl resins is similar, in general, to that customarily employed with liquid plasticizers of the ester type. The principal difference is that the resinous plasticizers, since they are high molecular weight compounds, do not exert the solvating effect of monomerics. They are as compatible as the monomeric plasticizers in the final product, but it requires more vigorous treatment to bring the vinyl polymer and resin plasticizer together.

Large-scale processors who use Banbury equipment, followed by mill refining before calendering, will find that only a slightly longer time and a higher temperature in the Banbury are required with the Paraplex resins.

On the other hand, where milling alone is involved, the longer time necessary for incorporation of Paraplex resins and the higher temperatures necessary to effect fluxing become quite apparent. When stocks containing resinous plasticizers are milled, it is advisable to blend the Paraplex in advance, using suitable heavy-duty equipment. After it has been fused and banded, the batch should be milled for a short time to insure complete homogeneity. The use of monomeric plasticizers with the Paraplex resins to facilitate milling is a common practice. The following mill roll temperatures are suggested for milling the Paraplex plasticizers with various vinyl resins.

Geon 101	310° to 320° F.
Geon 102	230° to 240° F.
Geon 202	230° to 240° F.
Vinylite VYNW	290° to 300° F.
Vinylite VYNS	230° to 240° F.

Page 5 of Defendants' Exhibit 23, Booklet entitled "Paraplex G-25," June 1944

THE RESINOUS PRODUCTS & CHEMICAL CO.

TABLE I — COMPARISON OF PARAPLEX G-25 WITH ESTER TYPE PLASTICIZERS IN VYNW

Plasticizer	Paraplex G-25	Dioctyl Phthalate	Tricresyl Phosphate	Dibutyl Sebacate
Tensile	2700	2650	3300	2100
Modulus at 100%	1648	1062	1438	540
Bend-Brittle Point ° C.[1]	−50	−50	−40	below −74
Volatility Loss %[2]	less than 0.1	less than 0.1	less than 0.1	9.8
Heat Stability[3]	6	3.5	3	5
Heat Deformation %[8]	11.0%	13.6%	18.0%	21.4%
Flammability[4]				
% Burned	4	100	0	100
Burning time (secs.)	4.1	19.1	2.4	17
Extraction Loss %[5]				
Water	less than 0.1	less than 0.1	less than 0.1	0.3
Nujol	less than 0.1	8.4	1.8	24.6
100 Octane Gas	2.4	—	22.6	—
Aromatic Fuel[6]	19.0	—	28.7	—

[1]Test specimens ½ inch x 6 inches x .080 inch stored 24 hrs. at −30° C. Specimens transferred quickly from cold box to methanol-dry ice bath with 5 minutes immersion for temperature equalization; then bent through 180° over ⅜ inch rod. Temperature of methanol bath lowered in 5° C. increments until specimen broke. The values above are those temperatures at which samples cracked.

[2]Volatility determined in circulating air oven. Stocks exposed 10 days at 60° C. Results reported as percent loss in original weight.

[3]Hours at 150° C. before appreciable discoloration or other change.

[4]Standard ASTM test (DTYI-41T) using .010 inch film and N/C fuse.

[5]Values expressed as percent loss in weight of original .010 inch film after 10 days' immersion at room temperature. Water changed 10 times, Nujol once, gasoline and aromatic fuel not changed during tests.

[6]AMS-3212 Fuel—contains 60 percent 100 octane gasoline, 20 percent toluol, 15 percent xylol, 5 percent benzol.

[7]Extraction loss of DOP and DBS in 100 octane gasoline and aromatic fuel not shown. It is well known that both of these plasticizers are almost completely extracted by such solvents.

[8]Improvised test which gives comparative values only. Stock subjected to load of 50 pounds per square inch for 1 hour at 120° C.

A161

Deft.'s Ex 24 id 2/16/55 MJS

Nov. 44

Title Page of Defendants' Ex. 24

PLASTICIZERS FOR USE WITH POLYVINYL CHLORIDE AND COPOLYMERS

THE RESINOUS PRODUCTS & CHEMICAL COMPANY
WASHINGTON SQUARE PHILADELPHIA 5, PA.

Page 2 of Defendants' Exhibit 24

Introduction

To be satisfactory for use with polyvinyl chloride or copolymers, any plasticizer must show the basic requirements of good compatibility and efficiency, as well as satisfactory water resistance and permanence. The outstanding plasticizers, in addition, will produce a compound showing such special properties as low temperature flexibility, oil resistance, non-flammability or low cost.

We feel that our various plasticizers may be classified in this second group and in each case, offer a unique combination of properties. As examples, we cite Dibutyl Sebacate for low temperature flexibility, Paraplex G-25 for oil resistance and non-migratory properties, and Plasticizer 35 for extremely low cost applications.

As a rule, the monomeric or elasticator types, when incorporated with polyvinyl chloride, are characterized by good plasticizing efficiency, good low temperature flexibility and poor resistance to plasticizer migration and extraction. In contrast, the polymeric or resinous types will show only fair plasticizing efficiency but excellent heat stability, permanence and unsurpassed resistance to migration and extraction. Most resins are incompatible with polyvinyl chloride and to our knowledge, Paraplex G-25 is the only one which is being used commercially.

For guidance the plasticizers are discussed as follows:

I. Monomeric or Elasticator Types

- A. Esters
  1. Dibutyl Sebacate
  2. Dibenzyl Sebacate
  3. Dioctyl Sebacate
  4. Dicapryl Phthalate
- B. Amides
  1. Plasticizer 35
  2. Plasticizer 36

II. Polymeric or Resinous Types

1. Paraplex G-25

The appendix follows the discussion of the individual plasticizers and discusses compounding and testing procedure in detail.

It will be noted that the formulations discussed herein, in most cases, involve the use of only one plasticizer. This does not mean to imply that binary or ternary systems are not to be considered. Commercial practice has proven that, in many systems, the use of a "compatibilizing" plasticizer will make possible the use of one showing desirable properties, or reduced cost, which otherwise could not be used. The use of Plasticizer 35 with Dicapryl Phthalate is a case in point. A complete study of such binary or ternary systems, however, is not within the scope of this booklet but we plan to have more complete data thereon in the future.

PATENTS

July 17, 1934	1,966,856
Oct. 31, 1939	2,177,627
June 1, 1943	2,320,442
Oct. 19, 1943	2,332,265
Oct. 29, 1946	2,410,089
Sept. 13, 1949	2,481,896
June 29, 1954	Re. 23,843

Patented July 17, 1934 1,966,856

UNITED STATES PATENT OFFICE

1,966,856

PLASTIC COMPOSITION

Frazier Groff, Charleston, W. Va., assignor to Carbide & Carbon Chemicals Corporation, a corporation of New York

No Drawing. Application August 10, 1931, Serial No. 556,300

10 Claims. (Cl. 106—22)

The invention relates to plastic compositions containing vinyl resins, that is, resins formed by the polymerization of certain vinyl compounds.

Vinyl resins of various types are known and various uses have been proposed for these substances. Previously prepared plastic compositions containing vinyl resins have not been uniformly satisfactory. It has been proposed to make improved vinyl resins by polymerizing a mixture of vinyl compounds, and by including other substances in the resins. These proposals have resulted in generally improved vinyl resins, but vinyl resins possessing the requisite uniformity of properties to make plastic compositions prepared from them economically successful have not been heretofore known.

The principal object of my invention is to provide a novel type of vinyl resins possessing uniformly desirable properties for the preparation of plastic compositions. Another object is to provide a novel molding composition containing vinyl resins, which is especially useful for forming phonograph or other sound records. Another object is to provide a novel plastic composition suitable for use as a wall or floor surfacing material, and still another object is to provide a novel moisture-proof packaging and insulating material.

The vinyl resins employed in my new plastic compositions are those which are obtained by the conjoint polymerization (by which is meant polymerization while in mutual contact) of a vinyl halide and a vinylester of an aliphatic acid. I prefer to use vinyl resins formed by the conjoint polymerization of vinyl chloride and vinyl acetate in the presence of a polymerizing catalyst. The preferred proportions by weight of vinyl chloride to vinyl acetate are 70% or more of vinyl chloride and 30% or less of vinyl acetate. Throughout the specification and the claims all the new compositions will be described on a percentage or parts by weight basis.

I have found by test that the vinyl resins above described are best suited to the formation of the plastic compositions of the present invention. However, not every vinyl resin formed by the conjoint polymerization of 70% or more of vinyl chloride and 30% or less of vinyl acetate is suitable for use in the new plastic compositions. The resins must further possess a high fusion point, low solubility, and must be tough, stable and resistant to heat. In order to make my novel plastics economically practical, the resins contained therein must be of uniform quality with respect to the properties set forth. A uniform vinyl resin of this type may be characterized by indicating the extent to which it is soluble in certain solvents, since this property is an accurate indication of the other properties of the resin. I therefore designate the vinyl resin which is preferred as an ingredient of my plastic compositions, as a resin resulting from the conjoint polymerization of vinyl chloride and vinyl acetate in the proportions of 70% or more of vinyl chloride and 30% or less of vinyl acetate, less than about 30% of the resin being soluble in cold (20° to 30° C.) toluene.

The preferred type of resins may be produced by causing a mixture of the vinyl compounds in the proportions thereof as set forth above to be polymerized in the presence of a suitable liquid medium, such as aliphatic paraffin hydrocarbons, aliphatic alcohols, and aliphatic ketones, and in the presence of a suitable polymerizing catalyst, such as benzoyl peroxide, at temperatures below about 60° C. The process of forming such vinyl resins does not form an essential part of the present invention.

In order to insure complete stability of the vinyl resin it is generally desirable to add to the resin a stabilizing substance or susbtances. In general, suitable stabilizing agents are basic in property and do not promote acid formation or oxidation. Examples of suitable stabilizers are: alkaline earth metal soaps, resinates, oxides, hydrates and carbonates; aromatic amino compounds which are water insoluble; other amines or ammonia and its substitution products generally. Specifically, calcium stearate, lime, the reaction product of calcium hydrate and manilla copal resin, ethyl toluidine, benzidine, tribenzyl amine, and the ethanolamines are preferred stabilizers. I have discovered that the preparation of light colored vinyl resin plastics is facilitated, and that the colors are more stable toward light, if titanium oxide or calcium carbonate, or both are included in the plastic composition.

The vinyl resin plastics may be readily prepared in permanent colors of any shade by the addition of dyes, lakes or pigments.

The above described vinyl resins which may be stabilized and colored as desired are the basic ingredients of my new plastics. Certain plastic compositions require the inclusion of filling materials. I have found that cellulosic or non-cellulosic fillers in various proportions may be used with the vinyl resins. Examples of cellulosic fillers are wood flour, cork, cotton flock, cotton linters and paper pulp; examples of non-

cellulosic fillers are barytes, silica, mica, asbestos, talc and rottenstone.

The plasticity of the plastic compositions may be altered and their flexibility and resilience may be varied by the addition of various plasticizers or modifying agents to the compositions. Typical plasticizers and modifiers are phthalic acid esters, halogenated napthalene derivatives, carnauba wax, certain rubber fractions, chlorinated diphenyl derivatives, tricresyl derivatives and glycol esters.

I am enabled to produce a wide variety of new plastic compositions by means of the above additions to the vinyl resins. The nature and properties of the plastic products are governed by the choice of ingredients and amounts thereof which are incorporated with the vinyl resin.

In general, plastic compositions which are adapted to the formation of molded objects by the application of thermo-plastic molding operations are prepared by incorporating from about 25 to 70 parts of a filling material and 1 to 5 parts of a plasticizer with from about 75 to 30 parts of the preferred vinyl resin, which may be colored and stabilized as desired. The molding compositions may be varied by using larger amounts of plasticizing materials, and molding lubricants may be used optionally. In some instances the unfilled resin may be used to form molded objects. For example, the unfilled resin, with or without plasticizers or modifying agents, and colored as desired, may be used to form dentures and the like.

Another type of plastic composition has as its basic ingredient a vinyl resin of the preferred type in conjunction with a large proportion of a plasticizing material. This composition may be formed into thin sheets and is useful as a moisture-proof, insulating packaging material. It may vary in thickness from 0.0004 inch to 0.250 inch and may be colored, opaque, transparent or translucent as desired. The sheets are very flexible and if suitable plasticizers are chosen, the plastics are resilient and flexible over a wide temperature range, including very low temperatures, i.e.—10° C. or lower. This material is useful not only as a protective or ornamental packaging material but as an electrical insulating material for use in cable, condenser and switchboard insulation.

If it is intended as a packaging material its attractiveness may be enhanced by including various odoriferous substances in the composition to produce a perfumed wrapping material. It may be easily cemented to form seals and joints by softening the sheet with a solvent for the composition and then applying pressure.

The plasticized flexible material may be incorporated with a filler, such as cork dust or asbestos, and secured to a fibrous backing, for example, burlap, to form a linoleum-like product suitable for covering floors and walls. This product may be formed either by hot pressing the plastic against the backing or by securing a preformed sheet of the plastic to the backing with an adhesive, such as a solution of a vinyl resin in acetone. The resultant product may be cut, bent, nailed and treated in the usual way as a floor-covering material, and possesses good wearing qualities. The plastic and filler may be mixed into a paste with a medium-boiling solvent and used as a troweling composition to fill joints in the floor or wall covering material. In this case the plastic is hardened by the evaporation of the solvent.

The compositions of my invention are substantially non-flammable as evidenced by the fact that a vinyl resin composition containing 50% of wood flour will not support combustion. Also, they are odorless, resistant to water, chemically inert and dielectric.

The following examples are illustrative of the invention:

I. A molding composition was prepared as follows:

50 parts of vinyl resin
30 parts of ground barytes
20 parts of rottenstone
0.5 parts of carnauba wax
0.5 parts of calcium stearate
0.5 parts of lime

The vinyl resin was prepared by polymerizing a mixture containing 80% of vinyl chloride and 20% of vinyl acetate in the presence of benzoyl peroxide, and was less than 25% soluble in cold toluene. The materials were mixed and milled to form a substantially homogeneous composition.

The composition is suitable for molding various articles, particularly phonograph records, both of the rigid and flexible type. The composition may be used to form phonograph records directly, or they may be formed by molding the composition over a flexible cellulosic or similar sheet. By the use of this composition it is possible to make flexible records having either one or two playing surfaces. The formation of these flexible records is facilitated because the use of solvents in applying the vinyl resin playing surface or surfaces is unnecessary, the coating being applied by a hot pressing operation. Rigid records formed from vinyl resin compositions may be produced in thicknesses down to about 0.025 inch and are characterized by unusual toughness and mechanical strength.

In every case the records produced possess a high degree of water resistance and resistance to atmospheric conditions. Also, the records are extremely resistant to needle wear and exhibit but slight wear on the needle. This latter property is shown by the fact that a single needle may be used to play a record formed from a vinyl resin composition 200 times before becoming worn sufficiently to require replacement, while by comparison, the same type of needle can be used to play records of the kind now commercially available but once before being worn to the same degree. The records formed from vinyl resins are also characterized by an extremely low surface noise level. This characteristic, together with the mechanical strength of the resin and the accuracy with which it may be molded, makes it possible to form records having more recorded sound per square inch of playing surface than is possible with records formed from other materials.

II. Another molding composition for general use, and for sound records, was prepared as follows:

500 parts of vinyl resin
5 parts of calcium stearate and lime
5 parts of carnauba wax
40 parts of fibrous talc
435 parts of cotton flock
25 parts of coloring materials

The vinyl resin of this composition was pre-

pared as described in Example I, and was about 88% insoluble in cold toluene.

III. A simple molding composition may be as follows:

200 parts of vinyl resin
200 parts of wood flour
8 parts of carbon black

The vinyl resin used in this composition was identical with that of Example I and was previously stabilized. The molding composition of this example is useful for forming molded objects of low cost. It produces objects which are hard but not brittle.

The molding operations by which these compositions may be utilized are the usual thermoplastic operations employing heat and pressure. For example, bars consisting of 31 grams of the composition of Example III were molded under 1900 pounds per square inch of pressure at 130° C. for 8 minutes. They were then cooled under a pressure of about 400 pounds per square inch. The molding conditions are dependent upon the molding composition, the object molded and upon each other, and are subject to wide variations. In general pressures from 200 to 2000 pounds per square inch may be used and temperatures of about 130° to 140° C. are preferred.

IV. A highly plastic composition was formed as follows:

100 parts of vinyl resin
60 parts of ethylene glycol monoethyl ether diester of ethylene glycol diphthalate
1 part of carnauba wax
1 part of calcium stearate
1 part of calcium hydrate

The vinyl resin was a product formed by the conjoint polymerization of 80 parts of vinyl chloride and 20 parts of vinyl acetate and was less than 30% soluble in cold toluene. The ingredients of this composition were mixed by fluxing on hot (100° to 120° C.) differential rolls, and the mix was sheeted out. This composition is well adapted as an ingredient of varnishes or lacquers and may be mixed with filling materials to form molded articles possessing a high degree of resilience and flexibility. Sheets of this composition retained their flexibility and discolored but slightly after 100 hours of exposure to the radiation from a mercury arc lamp at a distance of 20 inches from the bulb.

V. The composition of this example was composed of the following:

100 parts of vinyl resin
10 parts of diethylene glycol monophthalate previously neutralized with orthotoluidine

The resin used in this composition was the same as that of Example IV. The mixture was fluxed on differential rolls heated to 80° to 120° C. until a uniform mix was secured. This may be lubricated with carnauba wax and molded to form tough, flexible phonograph records having the desirable properties above described. If it is desired, filling materials, such as wood flour or barytes, may be added to this composition, and sheets of the filled material may be molded over paper to form flexible phonograph records. This type of record is especially adapted for use in forming reproducing records for home recording.

VI. A tough, plasticized composition was produced as follows:

100 parts of vinyl resin
10 parts of ethylene glycol monomethyl ether phthalate neutralized with tribenzylamine
1 part of carnauba wax
0.5 part of calcium stearate
0.5 part of calcium hydrate
100 parts of cotton flock

The vinyl resin was identical with the resin described in Example IV. The ingredients of this composition were mixed and then rolled on differential rolls heated to about 110° to 130° C. This composition is well adapted for surfacing soft cores, metal sheets, and the like by molding operations. The toughness of this composition is demonstrated by the fact that a nail was driven through the center of a disc 2 inches in diameter and ¼ inch in thickness molded from this composition without splitting or cracking the disc.

VII. An example of a floor covering material is as follows:

100 parts of vinyl resin
40 parts of ethylene glycol monoethyl ether diester of ethylene glycol diphthalate
140 parts of ground cork
70 parts of barytes

The vinyl resin was formed by conjointly polymerizing 80 parts of vinyl chloride and 20 parts of vinyl acetate, and was 85% insoluble in toluene at 25° C. The ingredients were thoroughly mixed by fluxing on heated differential rolls and formed into sheets. These sheets were then molded over burlap to form a linoleum-like product which possessed excellent wearing qualities.

VIII. Another floor covering material was prepared as follows:

310 parts of a 40% solution of vinyl resin in ethyl acetate
60 parts of ethylene glycol monoethyl ether diester of ethylene glycol diphthalate
3 parts of ortho-toluidine
100 parts of acetone
230 parts of approximately 6 to 8 mesh ground cork
2 parts of calcium stearate
3 parts of carnauba wax

These ingredients were thoroughly mixed and air-dried. The vinyl resin used was identical with the resin described in Example VII. The resulting mixture was a thick, viscous mass characterized by a crawling type of flow. A portion of this mix was distributed over burlap and the residual solvent was evaporated. This piece was then densified by a hot-pressing operation under a pressure of about 150 pounds per square inch. This material was very flexible and tough and resembled a flexible linoleum.

Another portion of this mix was dried to remove the solvent, distributed over a sheet of burlap and hot-pressed under a pressure of about 100 pounds per square inch. The product was very similar to that formed in the first operation.

IX. A troweling composition was formed by mixing

100 parts of vinyl resin plasticized with 30% of its weight of ethylene glycol monoethyl ether diester of ethylene glycol disphtalate
300 parts of acetone
150 parts of asbestos
20 parts of ground cork

When a uniform mixture had been obtained, it could be applied to any desired surface by a troweling operation. About 12 hours of air drying was sufficient to eliminate all the solvent and the resultant coating was tough, adhesive and resilient. It adhered well to wood, metal, burlap, paper, and the like. A smooth surface may be imparted to this coating by applying a surface coating of a vinyl resin solution. The resin used in forming this composition was identical with that used in Example VII.

X. A transparent flexible wrapping material was produced as follows:

100 parts of vinyl resin
20 parts of dibutyl phthalate
1.5 parts of carnauba wax
1 part of calcium stearate

The resin was produced by conjointly polymerizing 80 parts of vinyl chloride and 20 parts of vinyl acetate, and was about 75% insoluble in toluene at 25° C. These materials were fluxed on hot differential rolls and sheeted out in sheets of about 0.001 inch in thickness. These sheets are useful as a moisture-proof, non-flammable packaging material, or as an insulating material. The material is tough, flexible, resistant to heat and ultra-violet light, and possesses good tensile strength. It may be perfumed, colored, and produced in any thickness and degree of transparency.

XI. The process of forming the material of Example X may be modified by dissolving 240 parts of the composition of Example X in 400 parts of acetone and 200 parts of ethyl acetate. The solution is formed into sheets by pouring it onto a plate of polished metal, infusible phenolic resin plastic, or glass. The plasticized composition described has but slight tendency to adhere to the materials on which it is plated, and such tendency may be eliminated by lubricating the plate with a substance, such as carnauba wax. The sheets are suitable for use as wrapping or insulating materials, and may be formed into thicker or thinner sheets by pressing or calendaring the sheets which were originally formed.

From the foregoing description the method of practicing my invention and the uses of my new plastic compositions will be apparent. Modifications of the invention are possible and are included in my invention as defined by the appended claims.

I claim:—

1. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material, said vinyl resin being identical with that resulting from the conjoint polymerization of a vinyl halide and a vinyl ester of an aliphatic acid in the proportions of at least 70% of the vinyl halide and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

2. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material, said vinyl resin being identical with that resulting from the conjoint polymerization of vinyl chloride and vinyl acetate in the proportions of at least 70% of the vinyl chloride and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

3. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material, said vinyl resin being identical with that resulting from the conjoint polymerization of vinyl chloride and vinyl acetate in the proportions of about 80% of the vinyl chloride and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

4. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material and plasticizing material, said vinyl resin being identical with that resulting from the conjoint polymerization of a vinyl halide and a vinyl ester of an aliphatic acid in the proportions of at least 70% of the vinyl halide and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

5. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material and plasticizing material, said vinyl resin being identical with that resulting from the conjoint polymerization of vinyl chloride and vinyl acetate in the proportions of at least 70% of the vinyl chloride and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

6. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material and plasticizing material, said vinyl resin being identical with that resulting from the conjoint polymerization of vinyl chloride and vinyl acetate in the proportions of about 80% of the vinyl chloride and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

7. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material, and filling material, said vinyl resin being identical with that resulting from the conjoint polymerization of a vinyl halide and a vinyl ester of an aliphatic acid in the proportions of at least 70% of the vinyl halide and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

8. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material, plasticizing material and filling material, said vinyl resin being identical with that resulting from the conjoint polymerization of a vinyl halide and vinyl ester of an aliphatic acid in the proportions of at least 70% of the vinyl halide and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

9. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material and filling material, said vinyl resin being identical with that resulting from the conjoint polymerization of vinyl chloride and vinyl acetate in the proportions of about 80% of the vinyl chloride and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

10. A plastic composition comprising a substantial proportion of vinyl resin together with basic stabilizing material, plasticing material and filling material, said vinyl resin being identical with that resulting from the conjoint polymerization of vinyl chloride and vinyl acetate in the proportions of about 80% of the vinyl chloride and said vinyl resin being at least about 70% insoluble in toluene at 20° to 30° C.

FRAZIER GROFF.

Oct. 31, 1939. R. G. DREW 2,177,627

ADHESIVE SHEETING

Original Filed June 10, 1933

Fig. 1.

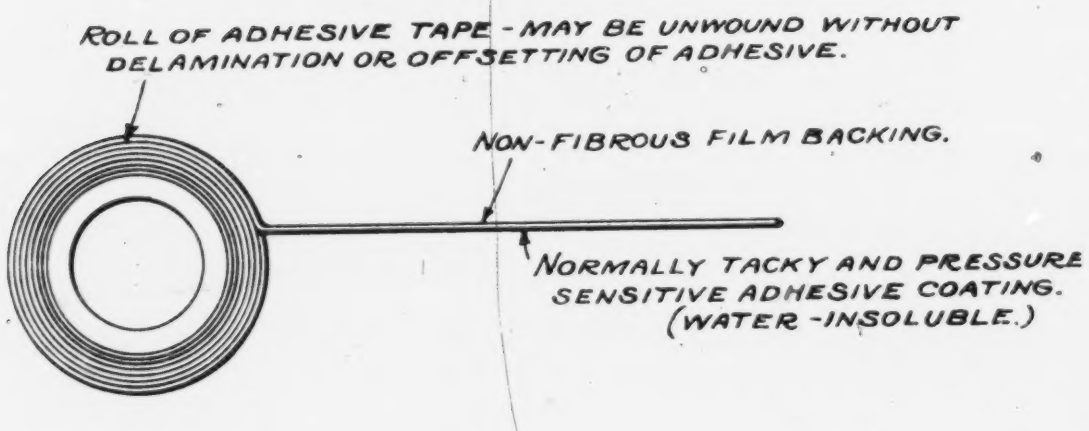


Fig. 2.

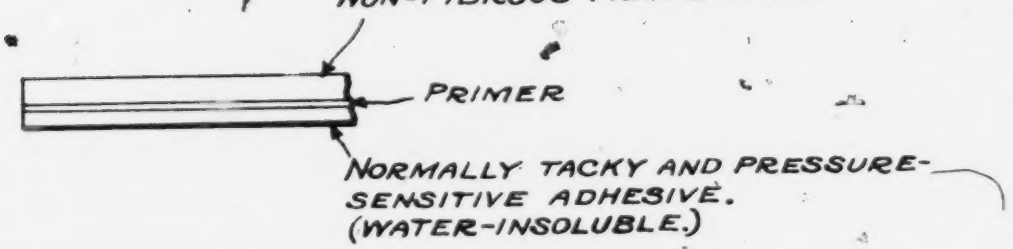
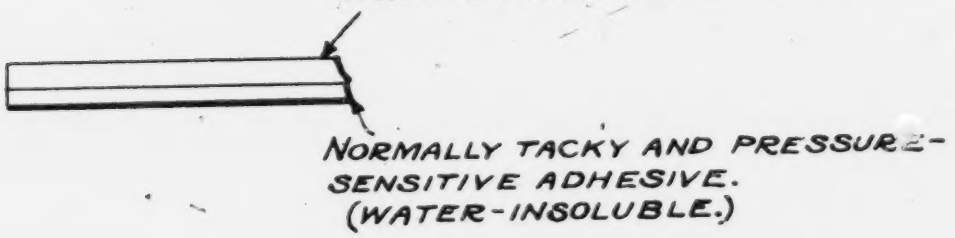


Fig. 3.



Inventor

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Patented Oct. 31, 1939

2,177,627

UNITED STATES PATENT OFFICE

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ADHESIVE SHEETING

Richard Gurley Drew, St. Paul, Minn., assignor to Minnesota Mining & Manufacturing Company, St. Paul, Minn., a corporation of Delaware

Original application June 10, 1933, Serial No. 675,291. Divided and this application February 18, 1938, Serial No. 191,259

16 Claims. (Cl. 91—68)

This invention relates to adhesive sheets having a backing with a non-fibrous surface (such as normal or waterproofed films of regenerated cellulose) and a coating of normally tacky and pressure-sensitive adhesive united thereto. While not limited thereto, the invention relates especially to transparent adhesive sheets, to adhesive sheets in the form of adhesive tapes which may be sold in stacked or coiled form, and to adhesive sheets or tapes which are well adapted to the sealing or securing of wrappers composed of non-fibrous lustrous cellulosic films and the like.

This application is a division of my co-pending application Ser. No. 675,291, filed June 10, 1933, and is in part a continuation of my co-pending application Ser. No. 534,386, filed May 1, 1931.

The development of packaging and wrapping sheets composed of thin, transparent and flexible non-fibrous films has raised special problems as to sealing or fastening with adhesives. Likewise, the desirability of using such films as backings for adhesive tapes cannot be met by use of the old conventional adhesives. Such sheet material is exemplified by gelatinized cellulosic materials which form films, such as regenerated cellulose, cellulose esters (as cellulose nitrate, cellulose acetate-butyrate and cellulose acetate), and cellulose ethers (as ethyl cellulose and benzyl cellulose), and by regenerated cellulose films which have been waterproofed by coating on one or both sides with a layer or film of a cellulose derivative. The popularity of these materials resides in such qualities as brilliancy, sheen and transparency, and in the later development of such material, in the quality of waterproofness. Ordinary glue type adhesives are insufficiently adherent by reason of the non-porous or highly glazed surfaces provided by this type of sheet material.

In accordance with this invention, sheets of such film material are provided with coatings of normally tacky and pressure-sensitive adhesive firmly united thereto. By "normally tacky and pressure-sensitive" it is meant that under ordinary atmospheric conditions the adhesive is stably in a condition such that it does not need to be activated by solvents or heat or otherwise prepared in order to secure good adherence to surfaces against which the adhesive coating (with its backing) may be pressed when used. An adhesive coating is provided which enables the adhesive sheeting to be affixed to smooth lustrous surfaces, such as non-fibrous cellulosic surfaces of wrapping or packaging sheets or films. An object of the invention is to provide a unified adhesive coating possessed of such coherence in relation to adhesiveness and so firmly united to its backing that the adhesive sheet may be stripped from smooth non-fibrous surfaces (not possessing special chemical affinity for the adhesive), to which it may have been temporarily applied, without offsetting of adhesive material. Hence the adhesive coating may be termed "non-offsetting", and this expression designates an important physical or physico-chemical property or characteristic of the adhesive coating, namely, that its coherency is greater than its adhesiveness. Further, an object is to provide adhesive sheets having an adhesive coating that is in elastic equilibrium with its backing so that warping and curling of the sheet, and blistering of the adhesive coating, are avoided.

In the accompanying drawing:

Fig. 1 shows a roll of adhesive tape, the tape having a non-fibrous film backing provided with a water-insoluble normally tacky and pressure-sensitive adhesive coating, which may be unwound without delamination or offsetting of adhesive;

Fig. 2 is a diagrammatic cross-sectional representation of a construction in which a primer coating is interposed between the backing film and the normally tacky and pressure-sensitive adhesive coating; and

Fig. 3 is a corresponding representation in which the primer coating is omitted.

Adhesive sheets are provided in which all components and the composite are transparent, so that the sheets may be applied without concealing the coloring or markings of the surfaces to which applied.

The transparent backing may be printed in reverse, on the face which carries the adhesive and prior to coating, to provide an adhesive sheet with the printing visible through and protected by the backing.

The adhesive sheets may be prepared with a surface continuously coated with adhesive, as in the case of ordinary adhesive tapes, labels and seals, or with the adhesive on certain areas only, as in the case of a packaging sheet provided with coated portions to permit sealing without the use of other sealing means.

It is preferred that the backing to which the adhesive coating is united be a transparent, flexible, non-fibrous film of gelatinized cellulosic material, such as regenerated cellulose (as normal or unwaterproofed "cellophane"), cellulose esters (as cellulose nitrate and cellulose acetate), cellulose ethers (as ethyl cellulose), or composites of such materials as, for example, a film of regenerated cellulose coated on one or both surfaces with a waterproofing film of a cellulose derivative (as a cellulose ester or ether). However, I may utilize backings comprised of materials other than gelatinized cellulosic materials, and which are either non-fibrous or are coated with non-fibrous films (preferably water-

proof) composed of cellulosic or other suitable material, including varnishes, lacquers, etc.

In its preferred form my invention is particularly applicable to transparent films of gelatinized cellulosic materials, such as regenerated cellulose, which is clear, transparent and lustrous. This may be made by forming an alkali cellulose compound, properly aged, of wood pulp or cotton liners, then xanthating to prepare viscose with carbon bisulfide and after careful filtration and clarifying by removing air or solid particles, casting the viscose in a coagulating bath of sulfuric acid and sodium sulfate. The film so cast is desulfurized, bleached, softened with glycerine, and then dried.

The regenerated cellulose film so produced may be waterproofed either on one side or on both sides, with a suitably compounded thin film of nitro-cellulose, cellulose acetate, cellulose ether, and similar cellulosic compounds. It will be understood that the waterproofing ingredients may include oxidized oils, varnishes and lacquers. The primary requisite is the application of these waterproofing films so as not to impair the lustrous and transparent characteristics of the sheet formed and to overcome any tendency to provide a warped sheet by the waterproofing layer that may be applied. Additionally, coatings such as transparent rubber, synthetic resins, and like materials may be used as a waterproof coating.

Where transparency of the adhesive tape is not of major importance, but where it is desired to provide a flat, unwarped exposed brilliant and lustrous surface, I have determined that an adhesive coating may be applied to the cellulosic film of the character previously enumerated and obtain a composite in which the adhesive is unified thereto, and in elastic equilibrium with the film, by using a composition made as follows:

Example A

A rubber compound and a tackiness augmenting agent in the form of a synthetic resin are used. Proportions suitable for ordinary temperate climates may comprise:

	Pounds
Plasticized, first quality plantation rubber, such as clear crepe or smoked sheets	10
Cumaron gum or resin	2
Zinc oxide pigment	½

The cumarone gum or resin is an artificial resinous material coming under the group name of cumarone and indene resins, which is the polymerization product of coal tar derivatives. The above ingredients are compounded on a rubber rolling mill to a plastic condition and then cut to desired body or consistency, using a rubber solvent such as benzol or a petroleum solvent, such as high test gasoline. In lieu of a synthetic resin, I may employ a low melting point natural resin, e. g., Burgundy pitch or pine oil foots. Burgundy pitch is soluble in both alcohol and benzol.

Example B

	Pounds
Plantation rubber	2
Mexican or wild rubber, high in natural resin content	5
Zinc oxide pigment	1

The ingredients above enumerated are compounded on a rubber mixing roll and then cut to the desired consistency in a rubber solvent, based upon the necessary viscosity for spreading this material.

It will be understood that the examples above given are for the purposes of getting the requisite adhesiveness in temperate climates. An increase in resinous material or wild rubber may be made for material to be used in colder climates, and in warmer climates the resin component may be reduced.

The resinous component may also be varied in its characteristics in its reactions to solvents by choice of the resinous material. Thus, for purposes of removal of the adhesive tape from some body to which it may be applied, the adhesive may be made so as to have a resin constituent which is soluble in a desired organic solvent, such as benzol, gasoline, acetone or alcohol. Thus, where it is desirable to make a surgeon's tape which is rendered removable by the application of alcohol, an alcohol soluble resin is added in the examples above cited. Such resin may be Burgundy pitch. This will permit alcohol to be used in removing a piece of adhesive tape from any surface, such as from the skin of a patient, by merely applying alcohol to the adhesive.

The rubber resin compounds in their solvents may be spread upon the backing directly, utilizing a knife spreader to uniformly and equally distribute this material upon the backing. The solvent may thereafter be removed by evaporation, preferably recovering the solvent by some suitable recovery method, leaving the rubber mixture upon the gelatinized cellulosic backing material. The coating so applied is firmly adherent and unified to the backing material and provides a normally tacky and pressure sensitive adhesive coating of a unified character, without in any way curling or warping the transparent gelatinized cellulosic film.

Where it is desired to obtain a clear composite of backing material and adhesive, the adhesive preferred by me for this purpose may be made as follows:

Example C

	Parts
Rubber (double break down latex crepe)	200
Para cumarone resin	85
Wood rosin	10
Liquid paraffin oil	5

(All parts are by weight.)

As a variation from the above, where lack of transparency is not objectionable and the addition of a colored hue to the composite of backing and adhesive material desirable, the formula may be varied as follows:

Example D

	Parts
Rubber (latex crepe)	250
Zinc oxide	225
Pine green light colored pigment	25
Wood rosin	137
Liquid paraffin oil	30

This type of adhesive is normally tacky and pressure-sensitive and has a greenish opacity. It will be understood that where a different color is desired to be imparted to the transparent film backing material, the pigmenting material may be correspondingly varied. Coloration in the adhesive may be used to neutralize or vary objectionable shades or colors in the transparent backing material.

If desirable, dyes may be used, particularly to preserve the transparency and attractive sheen of the composite, or the color (pigment or dye), may be added to the backing material itself. In either method of addition, where dyes are desir-

able and particularly for a clear blue transparency, indamine blue is suggested as of value for this purpose; pigmenting may be accomplished by such material as Prussian blue.

The zinc oxide filler, when used, serves as a reinforcing pigment imparting greater coherency and firmness to the adhesive coating. Colored pigments likewise function as reinforcing pigments and thus have a function in addition to that of coloring the adhesive.

In the examples C and D given above, paraffin oil has been included for purposes of plasticizing the rubber. I have found that in order to obtain maximum transparency and the highest possible bond strength and firmness of the adhesive inter se, the paraffin oil may be omitted.

Such adhesive coating, particularly valuable for this purpose, is as follows:

Example E

	Parts
Rosin	160 to 200
Thin latex crepe rubber	250
Beta naphthol	2.5

Approximately 3248 parts of benzol may be added to the above ingredients to provide a readily spreadable cement, and the ingredients may be incorporated in the benzol without the necessity for milling.

In the example given, beta naphthol has been specified and this is primarily used as an antioxidant. This material is desirable in the above formula, as well as in the other formulae given under A, B and C, in that the adhesives are given longer life.

Other antioxidants are desirable and may be included wherever rubber is used in the adhesive. Such antioxidants which may be used are as follows:

(1) Aldol-alpha-naphthylamine.

(2) Phenyl-beta-naphthylamine.

(3) Symmetrical-di-beta-naphthyl-para-diylene-diamine.

In the examples as above given, the proportions are by weight and variation may be made in the primary materials, as well as the quantity of the ingredients. Thus, in the examples given under C, D and E, latex crepe, the rubber component, may be varied by substitution in part or in whole by smoked sheet rubber. Though the synthetic resins, such as cumarone resins above referred to are preferred, various blends of other synthetic resins may be utilized, in part or in whole. To a certain extent, the wood rosin may be substituted by various grades of gum rosin.

In making the adhesives, the rubber base and the resin base determine the tackiness exhibited by the finished product. This relationship, also coupled to a certain extent with the treatment given to the rubber, determines this factor.

In producing a clear adhesive, the relationship of plasticizer (above listed in the form of liquid paraffin oil) and resinous material may be considered as constituting the tack producing phase of the adhesive and up to a certain point the greater the quantity of the tack producing phase that is added to the rubber, the greater the tackiness exhibited in the rubber base adhesive.

In general, for every two parts of rubber base, by weight, one part by weight of the tack producing phase may be added. As indicated above, the resinous content may be varied to increase or decrease the tackiness. However, in order to provide a unified adhesive, satisfactory for purposes of unwinding of the tape from rolls, the resinous content must be retained within certain limits beyond which the adhesive is likely to offset at normal atmospheric temperatures.

In the formulae above cited, double break down latex crepe rubber has been referred to and the treatment of this product alone, as well as the addition of the tack producing phase therewith, will control the characteristics of the adhesive layer. Thus, double break down latex crepe, as contemplated by me above, results from milling latex crepe rubber for approximately fifteen minutes to plasticize the same, with or without heat, and after aging for twenty-four hours, is again plasticized in a mill. At this stage, the material is suitable for addition to the material constituting the tack producing phase. This may be accomplished as follows:

Method A.—200 parts of rubber (double break down latex crepe from the rubber mill as above described) are placed in an internal mixer where the para cumarone resin, wood rosin and paraffin oil (where this is used) are gradually added during the mixing operation to thoroughly incorporate the same into the rubber. No solvent need be used if the mixer is powerful enough to knead these resinous materials into the rubber. When this dry mixing has been thoroughly accomplished, a rubber solvent, such as heptane or benzol, is introduced while the internal mixer is maintained in operation. This action is continued until complete solution results. The quantity of solvent added is in accordance with the means to be employed for spreading this material upon the backing material.

Method B.—200 parts of rubber (preferably double break down latex crepe as above made) are placed in a stirring equipment where paddles agitate the solvent and other ingredients into solution. When 200 parts of rubber have been placed into this mixer, the agitating member is started and a quantity of rubber solvent, such as heptane or benzol, is added to dissolve the rubber. The resinous materials in this particular example, para cumarone resin, wood rosin and the liquid paraffin oil (where this is used), are dissolved in a separate mixer, using an additional quantity of solvent, for example heptane or benzol. When these parts are uniformly distributed and in solution, the parts from each mixer are combined. The quantity of benzol or other solvent is calculated in accordance with the method which may be used for spreading it upon the backing material. The solvent is evaporated after coating or spreading of the adhesive upon the backing material.

In use, the adhesive as above described may be directly applied to the backing or sheets of transparent gelatinized cellulosic materials, previously enumerated, and forms a desirable product.

Where considerable unification is desired between the adhesive layer and the backing material, to assure proper anchorage of the adhesive layer with the backing material, thereby assuring satisfactory unwinding or separation when the composite is formed into rolls or stacks, it is preferred to first coat the sheet of gelatinized cellulosic material with a priming composition. Priming on one surface is particularly effective with sheets formed of regenerated cellulose. The priming operation consists of first coating the backing material before application of the adhesive materials previously described.

The priming composition as preferred by me is a solution of a rubber resin mixture in an or-

ganic solvent in which the solid materials may be varied from 15 to 50% with 85 to 50% of the solvents used. Preferably the solids constitute about 17% of the solution so prepared.

Primer No. 1

A preferred composition comprises:

	Parts
Rubber (latex crepe)	2
Resin (such as pine pitch or wood rosin)	4
A filler, such as whiting (optional)	1

These two or three ingredients, as listed, constitute the solid components in the priming mixture above enumerated.

It is preferred that the deposition product resulting from coating with the priming composition be one whose solid components retard the solvent action of the overlying material when coated thereon as a solution. That is, the solids which may be contained and are present in the primer composition are of such nature that after deposition they are difficultly soluble (only slowly dissolved) in the solvent used for plasticizing and coating the adhesive layer. In the example above given, such properties may be imparted to the deposition product by utilizing rubber which has been partially vulcanized, plasticizing in a mixing device such as an internal mixer in the presence of heat, sufficient to render the mass sticky and to cause the ultimate primer coating to have a strong bonding action. As an additional operation, a solvent retardent may be added. Though whiting is illustrated, other fillers may be used, such as zinc oxide, which serve as reinforcing pigments to give greater coherency and firmness, in addition to any solvent retarding action which they may have.

Though it is indicated that high grade vulcanized rubber, plasticized to tackiness, may be utilized with some degree of success in the example above cited and identified as Primer No. 1, it is preferred, particularly where transparency is desired, to use the combination of ingredients above identified, and to merely add during the mixing operation the requisite quantity of sulphur and accelerators. The quantity of these ingredients, if any, is merely sufficient to render the rubber component difficultly soluble in the solvent present in the solution of the adhesive composition, so made for spreading purposes, without reducing the quality of this priming coat to unify with the adhesive layer superimposed thereover.

Primer No. 2

Rubber, in the form commonly referred to as latex crepe, with the resin content in the proportions above indicated, has added thereto sulfur and accelerators. These are vulcanized with heat after intimate admixture and, while in the softened condition, are mechanically milled until a sticky mass, soluble in benzol or naphtha, is obtained. The amount of benzol or naphtha added is to obtain the requisite fluidity and these solvents may be added to the solid components in quantities of from 50 to 85% as compared with the rubber and resin content.

The primers above described under 1 and 2 may be further rendered resistant to the solvent action of the overlying adhesive to be applied in a subsequent step, by the use of "Vulcoloc" as a superimposed priming composition. This material is, to the best of my knowledge, a reaction product of rubber and a sulphur bearing acid. Vulcoloc may be applied directly to the backing material prior to the application of the solution of adhesive material. Application of an organic solution of the adhesive does not affect the coating of the Vulcoloc primer as applied.

A material which is suitable as a substitute for rubber in the primer, is an artificial or synthetic rubber known as "Duprene" ("Neoprene") which is a polymerized diolefine compound.

Additional examples of transparent primers which anchor the adhesive coating to regenerated cellulose such as Cellophane, whether waterproofed or untreated (ordinary), and to films of cellulose derivatives (such as cellulose acetate, cellulose nitrate and ethyl cellulose), etc., are as follows:

Primer No. 3

	Parts
Selected tube reclaim rubber	90
Latex crepe rubber	10
Whiting	40
FF wood rosin	140

Primer No. 4

Selected inner tube reclaimed rubber treated further to remove pigment	90
Latex crepe rubber	10
FF wood rosin	140

In the above examples, still better results will be obtained by using, in place of FF wood rosin, a heat-treated wood rosin known as "Solros" wood rosin.

The reclaim rubber and latex (and whiting or other reinforcing pigment when used) are compounded together on the ordinary type of rubber mill and milled for 30–40 minutes. This milled base is then transferred to a heavy duty internal mixer (such as a Baker Perkins Mogul type mixer) and milled for 1–2 hours with 10–20 lbs. steam pressure in the heating jacket. The rosin is then added and mixing is continued for another hour. The jacket steam is then turned off and the mass cooled. The requisite amount of solvent (heptane or benzol for example) is then added, preferably in amount equal to 4–5 parts by weight per part of reclaim rubber. Mixing is continued, generally for about ½ hour, until the whole mass is homogeneous. The resulting primer composition or solution is then ready for application to the backing.

In this method of compounding, the reclaim rubber becomes plasticized by the mechanical working in the presence of heat and air, and is further plasticized by the rosin which is thoroughly incorporated with the rubber.

The reclaim rubber is superior to raw rubber, for use in the primer, for several reasons, including: The primer coating is rendered difficultly soluble in the rubber solvent contained in the subsequently applied adhesive solution, because the reclaim rubber is in a partially vulcanized state which greatly decreases the rate of solution in rubber solvents. The primer coating has a greater bonding action, i. e., becomes more firmly unified to the backing and to the adhesive coating, due to the higher adhesion value of the reclaim rubber resulting from the heating cycle and amount of break down experienced in the reclaiming process. These features are obtained without sacrifice of firmness or coherency of the primer coating, due to the high cohesiveness of the reclaim rubber resulting from its prior vulcanization. If raw rubber were subjected to the same treatment, it would have softness and stickiness but would lack adequate cohesiveness.

The reclaim rubber above referred to in the

formulae for making the primers is preferably made as follows:

Light colored inner tube stock may be utilized, though other forms of culcanized rubber may be used. Where inner tube stock is used, it is chopped up on mill rolls, preferably of the type utilizing breaker members, simulating heavy gear teeth. Rolls of this character operate in pairs, the top one being free to move up and down, while the lower one is stationary. Relative rotation of these rolls serves to chop up the scrap. After the scrap is chopped and torn apart, it is fed to the breakers, which pulverize it further, whereupon it is then passed over a screen and the fine particles separated out. The coarse particles are recirculated through the breakers until they also go through the screen. The fine particles are then charged into horizontal digestors, where they are treated with caustic soda solution, the heating of the stock being carried out under a steam pressure of about 40 pounds while being agitated. This treatment is carried out from 8 to 24 hours, to remove all fibres and free sulfur, and to plasticize the rubber. After digestion as above described, the stock is washed with water until practically free from caustic. The stock is then charged into a continuous belt drying system, where it is dried at a rather low temperature. The stock is then ready for the mill room, where the first operation is to mass these small particles together on a large mill. After consolfdation on the large mill, the rubber is then run through refiners, which cause grinding and crushing of any hard particles in the stock. The product is then passed through a strainer in which the rubber is extruded through heavy mill screens into small rod-like forms, after which they are massed together into sheets or slabs.

In some cases the procedure above described may be slightly varied, for example, when certain types of inner tube reclaim are desired, the pulverized scrap is heated in the presence of steam alone, without any caustic. It is thereupon, after being heated, sent directly to the mill room, without any further treatment.

In general, the primer layer is one which makes satisfactory bond with the regenerated cellulose backing material, or the gelatinized cellulosic material constituting such backing material, which may include a waterproofing layer of cellulosic compounds. Such primer may be a layer of a synthetic resin, such as one of the group of polyhydric-alcohol polybasic-acid resins, which makes excellent union with gelatinized cellulosic materials and with rubber. In the event that it is desired to wholly eliminate the above types of primer layer and waterproof the backing material of regenerated cellulose, where this is used, the waterproofing layer over the regenerated cellulose backing material is one which has affinity for the adhesive coating so that the adhesive coating makes better anchorage than would be the case if the regenerated cellulosic film were used alone. Such waterproofing materials which have a primer function, may be a highly plasticized nitrocellulose or cellulose acetate, oxidized and gelatinized drying oils, synthetic resins, such as phenolic condensation resins, or those of water white characteristics, such as urea resins. Those ingredients are chosen, as above indicated, which will be difficultly soluble in the solvent used in the solution of the adhesive layer composition subsequently applied thereto, so as not to result in a weakened structure preventing proper unification between the adhesive coating and the backing material.

Where nitrocellulose is used for the waterproofing layer, it may be highly plasticized by resinous material, which may be used in the proportion of 67–50% to 33–50% of nitrocellulose material. The following is given as an example of a solution which when applied to the regenerated cellulose backing, will form a coating of this type upon evaporation of the solvents:

	Parts
Nitrocellulose, such as "½ second cotton"	9
Xylol	15
Cellosolve (ethylene glycol monoethyl ether)	10
Resin, such as "Rezyl 12" (a condensation product of castor oil and phthalic anhydride)	12
Dammar cut (a solution of 40% dammar resin and 60% benzol)	16

The method of application of the coating materials above described will, to a large extent, depend upon the character of the coating. The primer and adhesive coatings may be successively applied where these are used in solutions of volatile solvents, by an offset process from rollers uniformly coated with the primer compositions or the adhesive composition. With the more viscous composition of either primer or adhesive, these papers may be coated upon the backing by a knife spreader. For the more plastic form of either composition and where unification is desired, calendering or frictioning of these materials may be resorted to, to apply either the priming coat, or the adhesive coat or both.

As an example of one method which may be followed in preparing the composite, the following procedure is recommended. A web of regenerated cellulose film of the desired thickness (which may have been printed on the face receiving the primer) is carried through a set of vertically positioned squeeze rolls. The lower roll has transferred to it, or dips into, the solution of the primer composition. A uniform layer of primer is applied at this point to the film or web of backing material. The web thus prepared travels from the squeeze rolls, to a duct for removing and drying off the solvents in the primer. The web then is directed to a contrivance for coating, at which point a doctor knife or coating knife is used to spread a film of the composition of adhesive material. The composition is directly applied over the primer and the composite as coated is either hung in festoons or travels through a drying duct, at which point sufficient time is allowed for complete removal of the solvent, and to form the deposition product to the desired consistency, due to the solid components present, for tackiness. If heat has been utilized to separate the solvent from the deposition product resulting in the adhesive, the composite thus formed may be cooled and brought to room temperature, to render the product in more convenient form for stacking or winding into rolls. Where wound into rolls, the composite thus formed is then cut or converted into small rolls, suitable for trade requirements.

The adhesive composition as deposited upon the film as heretofore described is one which is normally tacky and pressure-sensitive. It is of particular utility in connection with the lustrous, highly polished backing material described, in that the adhesive layer is in equilibrium with it and will not alter or warp its appearance. As indicated, the adhesive layer is unified in that it

has great adhesion inter se (coherence) and when applied forms a unified product with the backing material. When wound into rolls or formed into stacks, the lustrous surface of the backing will not be modified, no offsetting will occur and ready separation is assured of the entire composite from its adjacent layer.

Where the product may encounter low humidities or low temperatures, it may be desirable to coat the back side of the backing material with a protective coating, such as a thin film of glycerine. In such event, a protective coating is applied which is not disintegrated by or which does not interfere with the adhesive action of the adhesive layer. It will be understood, however, that under ordinary conditions, the composite of backing material and adhesive layer as hereinbefore described is a complete unified product and no further treatment need be made.

The foregoing adhesive coatings are characterized by being water-insoluble and in themselves make for a waterproofing of the underlying base.

Primer No. 5

Casein	3 to 8 pounds, preferably 5 pounds
Water	9 to 40 pounds, preferably 30 pounds
Concentrated ammonium hydroxide	1 to 8 pounds, preferably 3 pounds
Rubber latex (preferably 60% concentration)	3 to 25 pounds, preferably 16 pounds

The characteristic features of the above primer are that it is compatible with the backing material where it is regenerated cellulose, such as Cellophane, flexibilized with glycerine, or such cellulosic material including the cellulosic compounds previously enumerated, coated with waterproofing materials, and is also compatible with any of the previously mentioned water-insoluble pressure-sensitive adhesive coatings.

In the formula of Primer No. 5, I have referred to the use of casein in connection with rubber latex. The casein is more or less water-soluble, especially in the presence of the ammonium hydroxide, and not only facilitates anchorage to glycerine-treated Cellophane when this is used as the backing, but is also compatible with the water-soluble type of adhesive coating when the priming coat is finally dried. This water-insoluble material, as included in the primer, may be supplemented by or substituted by glue, isinglass or gelatin, and other similar water-soluble materials, which not only facilitate the dispersion of the latex but also include the feature of being compatible with water-soluble materials. It will further be noted that though in the preferred form of the primer, where casein is used, it is preferred to use ammonium hydroxide in order to facilitate the solution of the casein, the quantity of ammonium hydroxide may be reduced where other water-soluble materials are used, and merely sufficient ammonium hydroxide is used to prevent untimely separation of the solids of the rubber latex.

The rubber included in the emulsion type of primer is for purposes of having some material compatible with the water-insoluble adhesive coating and water-insoluble backing, and while I have specified in my preferred form of primer the inclusion of a dispersion of rubber latex, dispersions of natural and synthetic resins, particularly those which will give a clear and colorless or water-white residium, may be substituted for the latex.

In general my emulsion type primer may be characterized as a double phase primer to the extent that it includes emulsified ingredients of both water-soluble and water-insoluble characteristics, in dispersed form.

It will be understood that in the application of the primer to the backing material, drying is effected after coating, before the adhesive coating is applied.

The use of water-soluble pressure-sensitive adhesive coatings is described in more detail in parent application Ser. No. 675,291, filed June 10, 1933, and in my companion application Ser. No. 191,261, filed of even date herewith.

The use of a plasticized rubber primer is claimed in my application Ser. No. 191,260; and the use of a cellulose-derivative backing in my application Ser. No. 191,264; both filed of even date herewith.

What I claim is as follows:

1. An adhesive sheet comprising a transparent flexible non-fibrous film backing having smooth lustrous surfaces and a non-offsetting normally tacky and pressure-sensitive water-insoluble adhesive coating firmly united to said backing, said adhesive including a coloring material visible through the backing so that the back surface has a lustrous colored appearance.

2. An adhesive sheet comprising a transparent flexible film backing having non-porous surfaces, and a flexible water-insoluble adhesive coating having a rubbery base and so composed that it is non-offsetting and normally tacky and pressure-sensitive, said adhesive coating being firmly united to said backing and the adhesive and backing being of such kinds that the back surface is inactive to the adhesive coating to a degree permitting unwinding of the adhesive sheet from rolls thereof without delamination or offsetting of adhesive, and the adhesive including a coloring material visible through the backing.

3. An adhesive sheet comprising a transparent flexible non-fibrous cellulosic film backing and a non-offsetting normally tacky and pressure-sensitive water-insoluble adhesive coating containing a reinforcing and coloring pigment firmly united to and visible through said backing, the back surface of the backing being lustrous and inactive to said adhesive coating to permit removal or unwinding from stacks and rolls without perceptible offsetting of adhesive.

4. A transparent adhesive sheet comprising a non-fibrous transparent flexible film backing having non-porous surfaces and a water-insoluble normally tacky and pressure-sensitive transparent flexible adhesive coating, said adhesive coating being firmly united to said backing and the adhesive and backing being of such kinds that the back surface of the backing is inactive to the adhesive coating to a degree permitting unwinding of the adhesive sheet from rolls thereof without delamination or offsetting of adhesive.

5. A transparent adhesive sheet comprising a non-fibrous transparent flexible film backing having non-porous surfaces and a water-insoluble transparent adhesive coating having a rubbery base and so composed that it is non-offsetting and normally tacky and pressure-sensitive, said adhesive coating being firmly united to said backing and the adhesive and backing being of such kinds that the back surface of the backing is

inactive to the adhesive coating to a degree permitting unwinding of the adhesive sheet from rolls thereof without delamination or offsetting of adhesive.

6. A transparent adhesive sheet comprising a non-fibrous transparent flexible cellulosic film backing having non-porous surfaces and a water-insoluble transparent adhesive coating having a rubbery base and so composed that it is non-offsetting and normally tacky and pressure-sensitive, said adhesive coating being firmly united to said backing and the adhesive and backing being of such kinds that the back surface of the backing is inactive to the adhesive coating to a degree permitting unwinding of the adhesive sheet from rolls thereof without delamination or offsetting of adhesive.

7. A transparent adhesive sheet comprising a non-fibrous transparent flexible regenerated cellulose film backing having non-porous surfaces and a water-insoluble transparent adhesive coating having a rubbery base and so composed that it is non-offsetting and normally tacky and pressure-sensitive, said adhesive coating being firmly united to said backing and the adhesive and backing being of such kinds that the back surface of the backing is inactive to the adhesive coating to a degree permitting unwinding of the adhesive sheet from rolls thereof without delamination or offsetting of adhesive.

8. An adhesive sheet comprising a transparent flexible non-fibrous cellulosic film backing having smooth lustrous surfaces and a water-insoluble normally tacky and pressure-sensitive non-offsetting transparent rubber-resin type adhesive coating firmly united to said surface, the composite sheet being transparent.

9. An adhesive sheet comprising a regenerated cellulose film having united thereto a waterproofing coating comprising a cellulose ester highly plasticized with a synthetic resin and providing a smooth non-fibrous surface, and a water-insoluble normally tacky and pressure-sensitive non-offsetting rubber-resin adhesive coating united to said surface, the parts of the composite adhesive sheet being transparent, and so firmly united together that the adhesive sheet may be unwound from rolls without delamination or offsetting of adhesive.

10. An adhesive sheet comprising a transparent flexible non-fibrous film having non-porous surfaces, a coating thereupon of a non-offsetting transparent normally tacky and pressure-sensitive water-insoluble adhesive, and an interposed transparent primer coating unified both to said surface and to said adhesive coating, the composite sheet being transparent and its parts so firmly united that it may be unwound from rolls thereof without delamination or offsetting of adhesive.

11. A transparent adhesive sheet comprising a non-fibrous transparent flexible film backing having non-porous surfaces, a water-insoluble transparent adhesive coating having a rubbery base and so composed that it is non-offsetting and normally tacky and pressure-sensitive, and an interposed transparent flexible primer coating firmly bonding said adhesive coating to the backing, the adhesive sheet having its parts so firmly united that it may be unwound from rolls thereof without delamination or offsetting of adhesive.

12. A transparent adhesive sheet comprising a non-fibrous transparent flexible cellulosic film backing having non-porous surfaces, a water-insoluble transparent adhesive coating comprised of raw rubber blended with a compatible tack-producing resin in proportions such that the adhesive coating is non-offsetting and normally tacky and presure-sensitive, and an interposed flexible transparent primer coating firmly bonding said adhesive coating to said backing.

13. An adhesive sheet comprising a transparent non-fibrous cellulosic film backing, a coating thereupon of a non-offsetting normally tacky and pressure-sensitive water-insoluble adhesive containing a coloring material, and an interposed transparent primer coating unified both to the backing and to said adhesive coating, the adhesive being visible through the backing and causing the back surface of the backing to have a colored appearance.

14. An adhesive sheet comprising a transparent flexible non-fibrous film backing, a coating thereupon of a non-offsetting normally tacky and pressure-sensitive water-insoluble adhesive containing a coloring material, and an interposed transparent primer coating bonding said adhesive coating to said backing, the adhesive being visible through the backing and causing the back surface of the backing to have a colored appearance.

15. An adhesive sheet comprising a non-fibrous flexible film backing having non-porous surfaces and a water-insoluble normally tacky and pressure-sensitive flexible adhesive coating, said adhesive coating being firmly united to said backing and the adhesive and backing being of such kinds that the back surface of the backing is inactive to the adhesive coating to a degree permitting unwinding of the adhesive sheet from rolls thereof without delamination or offsetting of adhesive, said adhesive sheet transmitting light so that the sheet will not conceal the coloring or markings of surfaces to which applied.

16. An adhesive sheet comprising a non-fibrous flexible film backing having non-porous surfaces, a water-insoluble normally tacky and pressure-sensitive flexible adhesive coating, and an interposed flexible primer coating firmly bonding said adhesive coating to the backing, the adhesive and backing being of such kinds that the back surface of the backing is inactive to the adhesive coating to a degree permitting unwinding of the adhesive sheet from rolls thereof without delamination or offsetting of adhesive, said adhesive sheet transmitting light so that the sheet will not conceal the coloring or markings of surfaces to which applied.

RICHARD GURLEY DREW.

June 1, 1943. A. E. MAIBAUER 2,320,442

ELECTROPLATING EQUIPMENT

Filed July 28, 1939

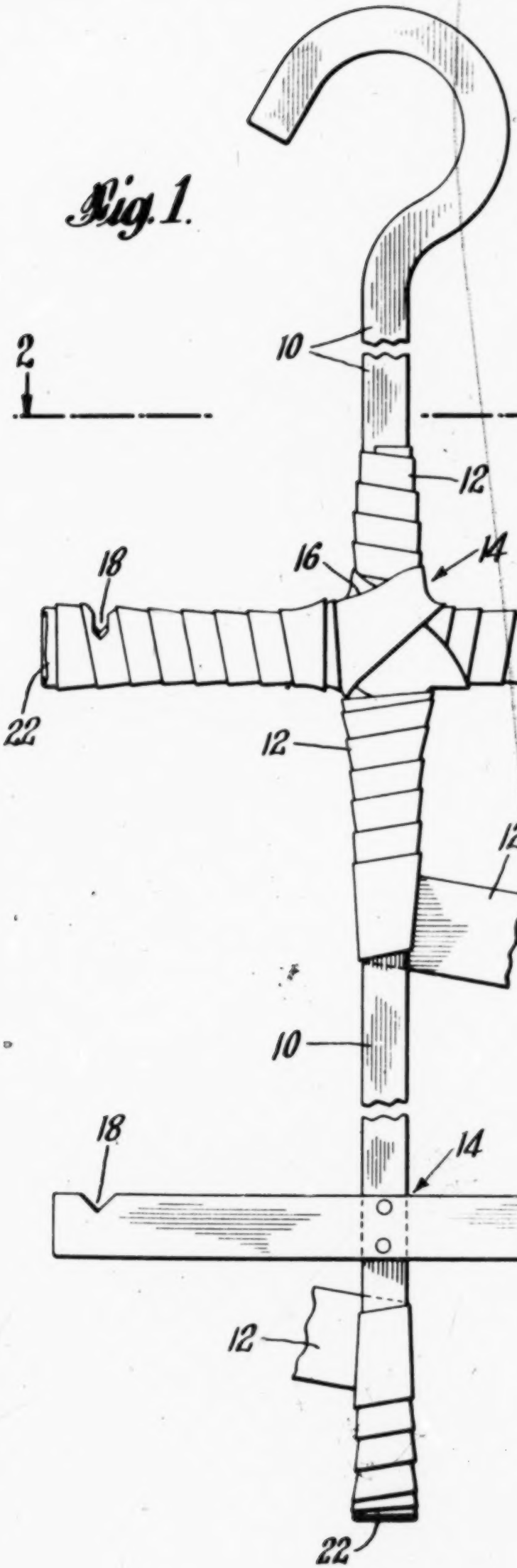

Fig. 1.

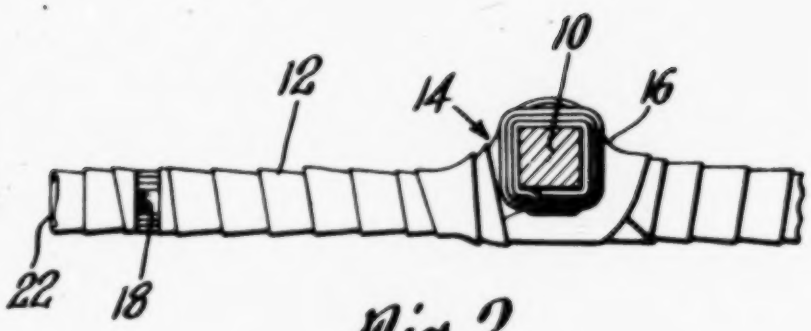

Fig. 2.

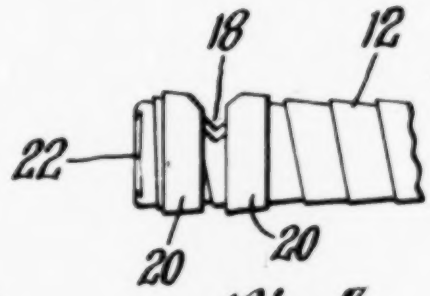

Fig. 3.

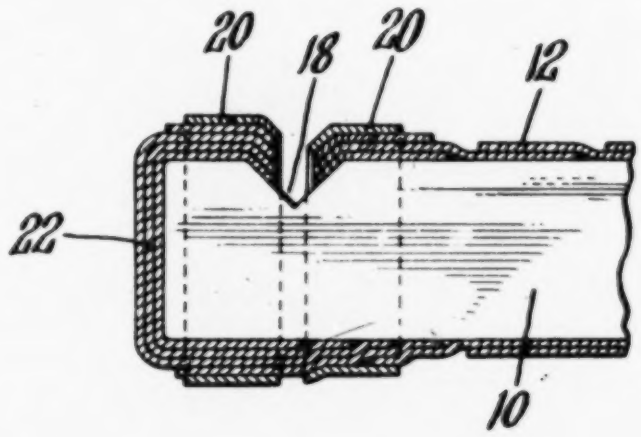

Fig. 4.

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2,320,442

ELECTROPLATING EQUIPMENT

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Application July 28, 1939, Serial No. 287,054

6 Claims. (Cl. 204—297)

This invention relates to the art of electroplating and electroplating equipment and insulation therefor.

From outward appearances the electroplating of an object is relatively simple as the object to be plated is merely suspended in a conducting bath of electrolyte and an electric current is passed between the electrodes, one of which is the article to be plated, whereupon the plating metal is deposited upon the article. In commercial practice, however, electroplating is a procedure which requires extremely close attention and fine regulation to produce an acceptable plated deposit in view of the complicated chemical reactions taking place within the electrolyte as well as at the electrodes; for example the composition of the electrolyte must be maintained within close limits and variations in the temperature, current density, etc. change the character of the deposit.

In commercial electroplating a number of the objects to be plated are frequently affixed to a rack of a conducting metal and the entire rack is immersed in the plating bath. It is a practical necessity that the racks be insulated else the plating process cannot satisfactorily be controlled and will be uneconomical as the plating metal will deposit on the rack which wastes the plating metal and current used to deposit it, shortly renders the rack unserviceable and renders it difficult for the plater to determine how much of a deposit has occurred on the articles which it was intended to plate. Among other difficulties, the metal of an uninsulated rack may dissolve in the plating bath and ruin it.

Various insulating media for racks have been tried and described in the literature. These include lacquers and it would seem relatively simple to insulate a rack merely by dipping it into an insulating lacquer or varnish or spraying or painting the lacquer on the rack and then permitting the coating to harden. In practice, however, lacquers leave much to be desired from the standpoint of economical application to the racks and operation of the racks after the lacquer is applied. Lacquers and varnishes usually contain volatile solvents for the gums or resins which deposit when the solvent evaporates, but the evaporation of the solvents may leave pin holes in the coating and thus numerous applications of the lacquer are frequently required and between each application it is often necessary to process the rack very carefully by air-drying and baking (see the United States patent to Herzog No. 2,072,170, March 2, 1937), as any solvent remaining in the coating will expand and form blisters which eventually disrupt the coating. Even with this care the coated rack is not as satisfactory as is desired since the coating may be uneven; it is difficult to apply an even coating by spraying or painting and when a dipped rack is hung up to drain the coating is always thinner on the upper parts of the rack and on the upper surfaces of the rack bars than on the lower. Thus a lacquer coated rack is not the ultimate in such devices.

With regard to the materials used for coating the racks there are numerous desiderata among which are that the coating material must not contaminate the bath and it must be as tough as possible, be substantially unaffected by acids or alkalis, have suitable electrical insulating properties and must maintain these characteristics at relatively high temperatures as well as at low temperatures. One of the most suitable bases for coatings is a copolymer of vinyl chloride or vinyl benzene and vinyl acetate containing from 50% to 95% of vinyl chloride or vinyl benzene and from 50% to 5% of vinyl acetate. Other vinyl halogen esters or vinyl aryl esters and vinyl esters of the lower aliphatic acids, that is acids containing from two up to five or six carbon atoms may be used. But even these basic materials require modification for the most satisfactory stop-offs. In practical electroplating the racks are subjected to a great deal of rough handling and temperature change and the insulation has to withstand all of these. For instance, the racks are subjected to abrasion when they are handled after insulating and during use and they are subjected to hot electrolyte and hot cleaning solutions and cold water washes, yet the insulation must not break through nor loosen from the rack during the handling nor may it crack when it is subjected to cold water while the metal of the rack is hot and in an expanded condition nor may it loosen from the rack when it is subjected to hot electrolyte while the rack is still cold and in a contracted condition. Another difficulty with using an unmodified vinyl copolymer is that the baked, unmodified copolymer is in a harder, more brittle and stiffer condition and the coated rack is less satisfactory for practical use.

The accompanying drawing shows a plating rack embodying my invention. In the drawing,

Fig. 1 is an elevation of a partially insulated rack;

Fig. 2 is a section on line 2—2 of Fig. 1, viewed in the direction of the arrows;

Fig. 3 is an elevation of an end of a cross arm of a plating rack, showing extra turns of tape at the end of the cross arm and at the contact point; and

Fig. 4 is an enlarged vertical section through the arm of Fig. 3.

According to one aspect of the present invention I overcome the difficulties experienced with prior stop-offs by covering the plating rack 10 with an insulating tape 12, the composition of which is important and includes the modified copolymers of vinyl compounds. The tape contains no readily volatile solvents and is not porous nor do pin holes develop in it; thus the electrolyte does not contact the rack. The tape is elastic and has elastic recovery so that when wrapped around the rack under tension, it contracts and presses against the parts of the rack with such pressure that the electrolyte cannot seep between the insulation and the metal of the rack. The tape also has such flexibility and yield that when it contracts onto the parts of the rack any irregularities in the rack, for instance nodules or tool marks are covered or filled in, thus permitting the use of a rack which is merely a rough casting or a roughly machined part. The tape is a decided improvement over a lacquer which would produce an extremely thin coating, if any, on the point of a nodule or on the ridge or burr left by rough machining. Furthermore, the preferred tape has the characteristic that one edge can stretch without stretching the other edge or can stretch more than the other edge and this, in conjunction with the elastic recovery, permits the tape to be wound around angles 14 in the rack and give a smooth non-puckering edge 16 on the short side of the turn. The elastic recovery of the tape also obviates the necessity of using primer coatings on the rack which have heretofore been required to make lacquers of the vinyl copolymers adhere to the metal of the rack, as the tape contracts around the rack bars and remains in place on the bars even though there is no primer. Another feature of the tape is that it does not lose its elasticity and elastic recovery even though heated and cooled and this is of distinct advantage when the racks are submitted to alternate heating and cooling as the tape will hug the metal of the rack and remain sealed against it when the rack is transferred between a hot electrolyte or cleaning bath and a cold wash water. A further advantage of a contractible tape is that at certain parts 19 of a rack, for instance where the article to be plated (or its support) makes electrical contact with the rack, it may be necessary for the insulation to be broken, and extra wrappings 20 of the tape may be applied next to these breaks to force the tape against the rack with greater than usual pressure to prevent the electrolyte from working in between the insulation and rack. In addition to the foregoing features a rack may be insulated more thoroughly, easily and quickly with tape than with lacquer. With a tape it is necessary only to wrap the rack with the tape, preferably with the edges of successive convolutions of the tape overlapping. This may be done very quickly and easily and all surfaces of the rack may be insulated equally and thoroughly whereas with a lacquer the tops of the rack bars and the points of the nodules as well as other parts where the lacquer runs off, have extremely thin insulating coverings. The tape may be and preferably is sufficiently thick, say from 5 to 15 mils, that a single wrapping on the majority of the rack is all that is necessary but a further advantage of tape as compared to lacquers is that several tape layers may expeditiously be applied where desirable, for instance where the breaks 18 in the insulation are necessary for contact purposes and at the corners 22 of the racks where abrasion and other mechanical injury may occur. An electroplating rack has been used to illustrate this phase of the invention but the tapes may also be used with other articles of electroplating equipment which are in the form of bars or tubes so that they may be wrapped and advantage taken of tapes as distinguished from lacquers and large sheets used to cover flat surfaces; in fact the characteristics of the tapes, previously referred to, which give them a decided advantage over lacquers on surfaces which can be wrapped are somewhat of a disadvantage or are of no benefit if large sheets are applied to flat surfaces as the sheets, if applied under tension, would draw away from the edges of flat surfaces leaving the edges exposed to the electrolyte, and also the elastic recovery of the material is of no advantage in holding a sheet against a plane surface to prevent electrolyte or cleaning solution from working in between the surface and the sheet.

With regard to the composition of the tapes, they are, as previously stated, based on the vinyl copolymers, but these require modification for the most satisfactory stop-offs to obtain the maximum desirable physical and chemical characteristics noted herein and a minimum sealing temperature. As the unmodified copolymers increase in molecular weight due to polymerization, thin films thereof become increasingly brittle and fragile and the unmodified copolymers also become increasingly hard, stiff and unworkable at ordinary temperatures, and their solubility decreases. If unmodified and in the state of polymerization where they are soluble they may be strong and non-brittle in thick molded pieces somewhat as glass is, but in thin films such as are deposited from lacquer they are quite fragile and easily break and shatter under a blow. Thus racks covered with lacquer films of the unmodified polymers cannot long endure the handling they receive in practical factory use. It is obviously desirable for the best stop-offs to retain the vinyl copolymers in their best operable condition for as long a time as possible. But it is necessary in modifying the vinyl copolymers that the modifying agents be such that they do not contaminate the electrolyte nor substantially affect the plating operation.

I have found that the group of modifiers suitable for admixture with the copolymers to give the composition the desired characteristics is rather limited. In general they should contain an aryl group or lead which contribute to inertness in an electroplating bath, or the phosphate radical which appears to do no particular harm to electroplating baths, or a radical which partakes of the nature of the copolymers. The modifiers should also be insoluble in water. Thus a modifier may be triphenyl phosphate (including thereby homologs) which combines aryl groups with the phosphate radical and is characterized by water insolubility, or an organic phthalate ester for instance a butyl, amyl, etc. phthalate or dibutoxy ethyl phthalate which contain an aryl group, or a lead salt or oxide, for instance lead stearate, lead oxide or lead abietate, which are quite inert, or cyclohexanol acetate which partakes of the nature of the acetate in the copolymer or chlorhydrin phthalate which partakes of

the nature of the chloride of the copolymer and also contains an aryl group.

It has also been found desirable to use a low molecular weight copolymer to modify a high molecular weight polymer. The low molecular weight polymers, when thoroughly incorporated with the high molecular weight polymers, do not render the high molecular weight polymers fragile as would ordinarily be expected but they do enable the overlapping edges of the tapes to seal against one another, this action being assisted by such modifiers as tricresyl phosphate which imparts a certain amount of adhesiveness to the tape particularly at elevated temperatures although leaving the surface substantially non-tacky at room temperatures. Thus the tape is characterized by such a dry surface at room temperature that it does not adhere to a person's hands and can easily be wrapped on a rack yet at elevated temperatures, say from 100° C. to 140° C. or when wet with an adhesive or a solvent for the low molecular weight polymer one surface of the tape will seal against an overlapping tape surface effectively to prevent leakage of the electrolyte between the surfaces. The mechanical contraction of one layer of tape on the other at room temperatures combined with the adhesiveness of the tape surfaces toward each other (even though substantially dry to a person's hands) is sufficient to seal against the electrolyte even at room temperatures but a substantially impervious seal is obtained under the influence of heat, adhesive or solvent as previously described.

Of the modifiers which may be used with the high molecular weight polymers, the low molecular weight polymers plastify the high molecular weight polymers and enable the tapes to seal without substantially affecting other properties, the tricresyl phosphate plastifies while increasing the tackiness of the surface as previously described, the lead compounds stabilize the mixture and the phthalates plastify while leaving the surface dry.

The foregoing and other objects and features of the invention will in part be obvious and in part will be pointed out in the following claims and description of a manner in which the tapes may be made and applied to electroplating racks. It is to be understood, however, that the description is for illustrative purposes only and that the invention is not to be limited strictly thereto.

In making the tape from 90 to 180 parts (by weight) of a copolymer containing 95% vinyl chloride and 5% vinyl acetate and a molecular weight from approximately 22,000 to 24,000, and from 350 to 630 parts of a copolymer containing 80% vinyl chloride and 20% vinyl acetate and a molecular weight of approximately 9,000 (molecular weights being calculated according to the Staudinger formula from dilute solutions of the resins) are thoroughly incorporated with from 140 to 266 parts of tricresyl phosphate, about 30 parts of lead abietate and from 32 to 61 parts of diamyl phthalate, the larger amounts of plastifying modifier being used with the larger parts of the high molecular weight vinyl copolymers to give tapes having such characteristics of elasticity, adhesiveness, softening temperature, etc. as are desired. After thorough incorporation, tapes may be formed from the mass either by extrusion, casting or milling. The tapes from 5 to 15 mils. in thickness and from ½ to 1½ inches in width have been found satisfactory in practical electroplating use but other thicknesses and widths may be used if desired.

In using the tape, the plating rack is merely wrapped with the tape having edges of the turns overlapping, preferably having a plurality of layers on the corners of the racks and on other parts where abrasion may occur as well as adjacent the non-insulated contact areas. While wrapping the rack the tape is preferably held under tension so that it is stretched and thus the tape contracts and presses tightly against the rack. Due to the ability of the tape to stretch more on one edge than on the other and to stretch more at the center than at the edges, a smooth and non-puckered covering may be had on the corners and where side bars join the main stem of the rack, even in the angles of the junctures the freedom from puckers permits a tight seal. After the rack is wrapped it may, if desired, be subjected to heat which softens the tape somewhat although it does not destroy the contraction of the tape on the rack bars. The softening of the tape combined with its contraction causes the overlapping edges to seal against each other. The heat may be applied in any suitable manner for instance by immersing the rack in hot oil or inserting in an oven for a few moments for instance 15 minutes at 245° F. or by fanning with a blow torch. The heat is preferably merely a flash heat sufficient to soften the tape and no prolonged air drying or baking to remove solvent is necessary or desirable and the covering is not porous after the heat treatment. The tapes offer a practical advantage in effecting repairs if the covering becomes broken; for instance a patch of the tape may easily be applied by pressing one end of a section of new repair tape on the old tape which is already on the rack, somewhat beyond the break. The new tape and the old may be united firmly by fanning with a blow torch. The patching tape may then be stretched tightly over the break or wound over the break and while held in position may be sealed in place with the blow torch. Repairs are thus effected very easily and quickly.

As the electroplating racks are almost invariably of metal which absorbs heat quite readily and the tapes do not conduct heat very readily, it will be seen that when a taped rack is subjected to heat, the highest tape temperature will be obtained at the overlapping edges of the tape where there are two thicknesses of tape and where sealing of the tape is desired.

If desired, the taped rack may be given a superficial treatment with a solvent for the low molecular weight component of the tape, for instance acetone or methyl ethyl ketone, or with a lacquer comprising a copolymer and a solvent. The solvent or lacquer softens the exposed overlapping edge and effects a seal but does not affect the tape to any appreciable depth. Thus the main body or interior portion of the tape is not affected and draws the overlapping edges together and any porosity resulting from the evaporation of the solvent is merely on the surface. The solvent or lacquer may be applied in any of the usual ways, for example by spraying, painting or dipping but dipping in a pure solvent or very thin lacquer is preferred and the rack should merely be plunged into the liquid and immediately withdrawn to wet the surface of but not soak the tape, and the solvent should be quickly evaporable as those mentioned above. It may here be remarked that if, for any reason, it is desirable to use a lacquer to coat parts of electroplating equipment, a solution of a soluble copolymer including the previously dis-

closed modifiers has been found to be better than the mere solution of the copolymer.

I claim:

1. Electroplating equipment to be subjected to electrolyte including a part insulated from said electrolyte with a stretched elastic tape consisting essentially of a plasticized copolymer formed from a vinyl ester of an aliphatic carboxylic acid having from two to six carbon atoms with a member of the group consisting of vinyl halides and vinyl benzene, said tape being wrapped under tension on the part with the turns overlapping, the insulation on said part being substantially impervious to said electrolyte.

2. Electroplating equipment to be subjected to electrolyte including a part insulated from said electrolyte with a stretched elastic tape consisting essentially of a plasticized copolymer of vinyl chloride and vinyl acetate, said tape being wrapped under tension on the part with the turns overlapping, the insulation on said part being substantially impervious to said electrolyte.

3. Electroplating equipment to be subjected to electrolyte including a part insulated from said electrolyte with a stretched elastic tape consisting essentially of a plasticized copolymer formed from a vinyl ester of an aliphatic carboxylic acid having from two to six carbon atoms with a member of the group consisting of vinyl halides and vinyl benzene, said tape being impervious to the electrolyte and wrapped under tension on the part.

4. Electroplating equipment to be subjected to electrolyte including a plurality of parts in angular relation to each other and wrapped stretched elastic tape insulation on said parts, said tape consisting essentially of a plasticized copolymer formed from a vinyl ester of an aliphatic carboxylic acid having from two to six carbon atoms with a member of the group consisting of vinyl halides and vinyl benzene, said tape being wrapped on said parts under tension, and the insulation including the copolymer being substantially impervious to said electrolyte and insulating said parts from said electrolyte.

5. Electroplating equipment to be subjected to electrolyte including a part insulated from said electrolyte with a stretched elastic tape consisting essentially of a mixture of high and low molecular weight copolymers formed from a vinyl ester of an aliphatic carboxylic acid having from two to six carbon atoms with a member of the group consisting of vinyl halides and vinyl benzene, said high molecular weight copolymer having a molecular weight between approximately 22,000 and 24,000, said low molecular weight copolymer having a molecular weight of approximately 9,000, said tape being wrapped on said part under tension, and the insulation including said copolymers being substantially impervious to said electrolyte.

6. Electroplating equipment to be subjected to electrolyte including a part insulated from said electrolyte with wrappings of a stretched elastic tape consisting essentially of a plasticized copolymer formed from a vinyl ester of an aliphatic carboxylic acid having from two to six carbon atoms with a member of the group consisting of vinyl halides and vinyl benzene, a substantially water insoluble plastifier for the said copolymers and a stabilizer for the said copolymers, said plastifier and stabilizer being substantially free from deleterious effect on the electrolyte, said tape being wrapped on said part under tension.

ALBERT E. MAIBAUER.

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UNITED STATES PATENT OFFICE

2,332,265

ADHESIVE SHEETING

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No Drawing. Application June 27, 1941, Serial No. 400,145

5 Claims. (Cl. 117—122)

This invention relates to flexible sheeting coated with a pressure-sensitive adhesive and pertains specifically to a transparent tape made from plasticized gamma polyvinyl chloride coated with an adhesive composition comprising polyisobutylene, rubber, and a resinous material.

Pressure-sensitive adhesive tapes with paper or fabric backings have long been known, but it has been hitherto impossible to find an adhesive which is satisfactory for use with a plasticized gamma-polyvinyl chloride backing. There are many advantages to be gained by using polyvinyl chloride, or a polymer in which vinyl chloride is the principal constituent such as a copolymer of vinyl chloride with minor proportions of vinyl cyanide, vinyl acetate or other vinyl ester, vinylidene chloride, or the like. A backing made of one or more of these materials is, without further treatment, waterproof, non-inflammable, resistant to oils and solvents commonly used in paint or lacquer, and extremely resistant to aging by sunlight or air. Moreover, tape made from this material may be produced in a variety of colors, and may be transparent, translucent, or opaque. Because of the high tensile strength of plasticized gamma polyvinyl chloride the film used as backing may be extremely thin without danger of having the tape tear when being removed from a surface to which it has been applied.

I have found that pressure-sensitive adhesives which give satisfactory results with paper or fabric backings are not effective with backings made from plasticized gamma-polyvinyl chloride. Ordinary adhesives either do not adhere well to the polyvinyl chloride backing, or, if they do adhere, they tend to off-set; that is, when the tape is rolled up on itself the adhesive layer tends to stick to the back of the tape below it rather than remain fixed to the face of the tape. Moreover, if the tape made with this adhesive remains rolled up on itself for a few days it develops wrinkles which extend through the backing and destroy the desired appearance.

I have now discovered that a satisfactory pressure-sensitive adhesive tape can be made by combining a backing of plasticized gamma-polyvinyl chloride or other polymer in which the principal constituent is vinyl chloride with an adhesive comprising rubber, a resinous material, and polyisobutylene.

The backing sheet may be made by any of the usual methods—e. g., extrusion, molding, calendering, or by rotating a heated cylinder partly immersed in a solution of the desired polymer and plasticized in a volatile solvent, and stripping the resultant film from the cylinder as it rotates. The thickness of the backing sheet may vary over a wide range, depending upon the particular use to which the tape or sheeting is to be put. In general, thicknesses of .001 to .004 inch or more are satisfactory. Any of the usual plasticizers may be used with the polymer, but more than about 20% by weight of the plasticizer, based on the weight of the polymer, produces a sheet which is too soft to be useful. Plasticizers such as tricresyl phosphate, dibutyl phthalate, dioctyl phthalate, tributyl aconitate, butyl phthalyl butyl glycollate and the like all give satisfactory sheets. Any of the pigments or dyes commonly used in the rubber or plastics industries may be incorporated in the backing composition to provide a variety of effects. In order to increase the stability of the polymeric composition toward sunlight and ultraviolet light it may be desirable to add small amounts of stabilizers such as calcium stearate, calcium silicate, lead silicate, partial esters of polyhydric alcohol and unsaturated fatty acids, triethanolamine, and the like.

Although the rubber, polyisobutylene, and resinous material of the adhesive layer are all essential ingredients, their relative proportions may vary over a fairly wide range. In general, about 50 to 75% by weight of milled rubber, 15 to 30% of polyisobutylene, and 5 to 15% of resinous material are desirable. The rubber should be well milled or plasticated before using, and may be either natural or a synthetic such as a copolymer of butadiene with another copolymerizable monomer. The polyisobutylene should preferably be a material with a moderately long chain-length, although other materials are also satisfactory. Such compounds as the oily material sold as Vistac or the rubbery material sold as Vistanex are suitable. The resinous material is preferably an ester gum, although other materials such as melted rubber, rosin, or the like may be used. It is usually preferable to apply this adhesive to the backing in the form of a solution in a volatile solvent such as gasoline, hexane, benzene, or mixtures of these materials with each other or with other hydrocarbon liquids. The solution may be applied by spreading, spraying, or any other suitable method.

As a specific example of my invention I have prepared a backing containing 100 parts of gamma polyvinyl chloride, 5 parts of dioctyl phthalate, and 2 parts of the monoester of glycerine and cottonseed fatty acid. A polished metal drum heated to a temperature of about 150° C. is rotated through a 10% solution of this composi-

tion in cyclohexanone. The transparent film produced is about .002 inch thick and is stripped from the drum before the completion of its revolution. This film is then coated on one side by means of a spreading machine with a solution of 20 parts of milled rubber, 7 parts of the rubbery polyisobutylene sold as Vistanex and 3 parts of ester gum in 10 parts of benzene and 80 parts of gasoline. After drying at a temperature between 30° and 50° C. or more the product may be rolled up on itself and cut to tapes of the desired width.

Tape such as this has not only the desirable feature of transparency and glossy surface, but also is extremely resistant to deterioration from light, heat, oils, solvents, and many corrosive chemicals.

I claim:

1. A pressure-sensitive adhesive sheet comprising a backing consisting substantially of a plasticized polymer in which the principal constituent is vinyl chloride, and an adhesive layer consisting of rubber, polyisobutylene, and a member of the class consisting of melted rubber, rosin, and ester gum.

2. A pressure-sensitive adhesive sheet comprising a backing consisting substantially of a plasticized polymer in which the principal constituent is vinyl chloride, and an adhesive layer consisting of rubber, ester gum, and polyisobutylene.

3. A pressure-sensitive adhesive sheet comprising a backing consisting substantially of plasticized gamma-polyvinyl chloride and an adhesive layer consisting of rubber, ester gum, and polyisobutylene.

4. A pressure-sensitive adhesive sheet comprising a backing consisting substantially of plasticized gamma-polyvinyl chloride and an adhesive layer consisting of rubber, polyisobutylene, and a member of the class consisting of melted rubber, rosin, and ester gum.

5. A transparent pressure-sensitive adhesive sheet comprising a backing consisting substantially of plasticized gamma-polyvinyl chloride and an adhesive layer consisting of 20 parts of milled rubber, 7 parts of polyisobutylene, and 3 parts of ester gum.

RICHARD F. SCHMIDT.

Patented Oct. 29, 1946 2,410,089

UNITED STATES PATENT OFFICE

2,410,089

PRESSURE-SENSITIVE ADHESIVE TAPE

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No Drawing. Application August 17, 1944, Serial No. 549,963

8 Claims. (Cl. 117—122)

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This invention relates to an improved pressure-sensitive adhesive sheet, conveniently in the form of an adhesive tape, having a flexible unified paper backing provided with a coating of eucohesive pressure-sensitive adhesive. By eucohesive is meant that the adhesive is more cohesive than adhesive, but still tacky.

Paper backings for pressure-sensitive adhesive tapes have previously been unified with impregnating compositions comprising broken-down rubber and rosin. Such compositions adhere well to paper fibers, are high in internal strength, are sufficiently compatible with lacquer solvents and the like so that lacquer deposited upon the back surface of the finished tape will be held thereon and will not run off onto the adjacent margin of the area being lacquered, and in general are such as to produce adequately unified and otherwise desirable paper backings for pressure-sensitive adhesive tapes.

However these prior art unified backings, being somewhat sensitive to lacquer solvents, do not possess a high degree of resistance to solvent penetration, or of "bleedproofness", i. e. resistance to the penetration through the backing of coloring material from colored lacquers. Furthermore the impregnation of the paper being usually carried out from hydrocarbon solvents adds to the expense of the operation and creates explosion hazards which require extra precautions and equipment.

Paper backings for pressure-sensitive adhesive tapes have also previously been unified by impregnating with aqueous solutions of glue plasticized with glycerine. Such backings are for all practical purposes entirely resistant to penetration by lacquer solvents but possess the disadvantage of being sensitive to changes in humidity.

Vinyl acetate is a readily available low cost and hence highly desirable raw material which may be polymerized, either alone or together with other unsaturated and polymerizable materials, to form synthetic polymers. Polyvinyl acetate alone is a hard, tough solid which may be plasticized with various suitable liquid plasticizers to form soft masses which might be used for the unification of paper. But these compositions, due to the migration of the plasticizer from the vinyl acetate polymer, may cause softening and weakening of pressure-sensitive adhesive films in contact therewith, and hence are not satisfactory for use in unified paper backings for pressure-sensitive adhesive tape. Vinyl acetate has been copolymerized with methyl and ethyl esters of maleic and fumaric acids, but these copolymers

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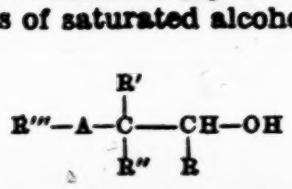
are even less flexible than unmodified polyvinyl acetate and are likewise unsuited for the unification of paper backings for pressure-sensitive adhesive tapes because of the necessity of plasticizing with liquid plasticizers.

We have now found that certain strong, flexible, adherent synthetic polymers prepared by the copolymerization of vinyl esters such as vinyl acetate with certain neutral esters of ethylene-alpha, beta-dicarboxylic acids may be utilized without addition of plasticizers or other deleterious compounding ingredients for the impregnation and unification of paper backings for pressure-sensitive adhesive tapes. These neutral esters are esters of saturated alcohols having the formula:



in which R, R′ and R″ are hydrogen atoms or saturated alkyl groups, A is oxygen, methylene, or an alkyl methylene group, and R‴ is a saturated alkyl or alkoxyalkyl group. Tertiary alcohols are not suitable for this work because their esters are too unstable when heated. Secondary alcohols, where R is an alkyl group, are of somewhat less interest than primary alcohols, where R is hydrogen. The alcohols used should be saturated, that is, they should contain no carbon to carbon double bonds, since ethylene-alpha, beta-dicarboxylic acid esters of unsaturated alcohols would give excessive amounts of cross-linking when copolymerized with the vinyl ester. Di- or polyhydric alcohol esters, being di- or polyfunctional would likewise give excessive amounts of cross-linking when copolymerized with the vinyl ester. However, small amounts of these or other cross-linking agents may be used in combination with the principal monomers, with advantageous results.

The neutral esters to be copolymerized with vinyl acetate are readily prepared by heating a mole of maleic acid or anhydride or of fumaric acid with an excess (more than 2 moles) of the alcohol or alcohols to be used, together with a small amount of acid catalyst, to a temperature above 100° C., and removing the water formed during the reaction by distillation. Para-toluene sulfonic acid is the preferred catalyst for this esterification and it is generally used in amounts ranging from ½–2% based on the maleic acid or anhydride or fumaric acid. In the case of alcohols which are immiscible with water, it is a very simple matter to distill

alcohol and water from the reaction mixture, separate the water and return the alcohol to the reaction vessel. In the case of 2-ethoxyethanol, the water formed during the esterification may be removed through a fractionating column. Benzene, toluene, heptane or other volatile, water-immiscible solvents may be added to the reaction mixture to aid in the removal of water if desired. In this way the reaction is readily carried to completion. The excess alcohol, and the volatile solvent if any is used, are removed by distillation and the product may be used for polymerization in this crude form, or it may be purified by washing with a dilute aqueous alkaline solution to remove the catalyst and any unesterified acid, or by distillation under reduced pressure.

In those esterifications starting with fumaric acid, esters of fumaric acid are obtained. When maleic acid or anhydride is used as the starting material the conditions of esterification generally cause some of the maleic acid products to isomerize into corresponding fumaric acid derivatives so that the final product obtained consists of a mixture of the two. It is believed, however, that the amount of fumaric acid ester present in the products prepared from maleic acid or anhydride is small, and accordingly in this specification esters prepared from maleic acid or anhydride are referred to as maleates. The maleate esters may be more completely converted into fumarate esters if desired by any of the common methods, such as by treatment with secondary amines, light, heat, acids, etc.

Commercial vinyl acetate which has been distilled to free it of inhibitor is suitable for these polymerizations. It should be free from excessive amounts of acetaldehyde since the presence of acetaldehyde tends to inhibit the polymerization and to lead to low molecular weight products.

The copolymerizaton of vinyl acetate with these maleic acid and fumaric acid esters is readily carried out by any of the common methods of polymerization. The method of most interest in the preparation of thees copolymers is the so-called emulsion method whereby these products are obtained in a dispersed form. These dispersions are of interest for use directly in the impregnation of paper since this eliminates organic solvents which would increase the cost of operation and introduce explosion hazards. By using such aqueous dispersions it is also possible to use copolymers so highly cross-linked as to be completely insoluble in organic solvents. These dispersions are usually prepared with a solids content of 30–60%.

Any of several commercial emulsifying agents may be used in the preparation of these dispersions, including long chain alkyl sulfate salts, alkyl substituted aryl sulfonic acid salts, soaps and salts of long chain amines. A small amount of a protective colloid may be added to stabilize the dispersion; methyl cellulose, gelatin, methyl starch, polyvinyl alcohol, sodium alginate, and the like may be used. Any of the various water soluble peroxide type catalysts, such as ammonium persulfate, potassium persulfate, hydrogen peroxide or sodium perborate may be used, usually in amounts of 0.1–2%, based on the monomers. The pH during polymerization is generally maintained between 4 and 7. The use of a pH appreciably higher than 7 is to be avoided since an excessive amount of vinyl acetate is hydrolyzed during the polymerization at elevated pH. The polymerizations are generally run at a

temperature of between 50° C. and the temperature at which the reaction mixture refluxes gently, although other temperatures may also be used. It is generally preferred to carry out the polymerization at the lowest temperature which will still give an economical rate of reaction since this gives higher molecular weight products. In general, it is possible to complete these polymerizations in from 1 to 6 hours, depending on the composition of the monomers, concentration, amount of catalyst and temperature employed.

By copolymerizing vinyl acetate and maleate or fumarate esters with small amounts of acrylic acid it is possible to prepare dispersions which are very stable to mechanical action and which have a very small particle size. Since acrylic acid is difficult to isolate in pure form it has been found convenient to hydrolyze methyl or ethyl acrylate with an equivalent amount of sodium hydroxide solution to give a sodium acrylate solution. Such a sodium acrylate solution does not polymerize and yields acrylic acid readily on acidification. In order to get the acrylic acid to copolymerize uniformly with the vinyl acetate and maleate or fumarate esters it is necessary to control the pH of the polymerization mixture. In general it is preferred to carry out the polymerization in the presence of these acrylates at a pH between 3.5 and 6. Other equivalent polymerizable carboxylic acids may be substituted for the acrylic acid.

These polymerizations may also be carried out by other known methods, for example the granular method, and the resulting polymers may be dispersed or dissolved in water or organic solvents for use in the impregnation of paper.

We have found that copolymers which have most desirable properties as impregnants and unifying agents for paper backings for pressure-sensitive adhesive tapes have a modulus of elasticity of between 4 and 15 megadynes per square centimeter, although copolymers having a modulus of as low as 2½ or as high as 25 megadynes per square centimeter may be used in some instances. At values lower than 2½ the polymer is too soft and the impregnated paper is not sufficiently unified; at values higher than 25 the polymer is too stiff and the impregnated and unified paper is harsh and brittle.

The modulus of elasticity as here referred to and as specified in the claims is calculated from the stress at 10% elongation as determined on a thin film of the copolymer tested at 25° C. in a Scott Inclined Plane Serigraph, or an equivalent testing apparatus, wherein the time required to obtain 10% elongation is in the range of approximately 1 to 4 seconds.

In many cases, it is desirable to add 0.1–3.0% of a polymerizable material containing two or more polymerizable groups per molecule to the reaction mixture to get a cross-linked copolymer. The use of such a cross-linking agent decreases the solubility of the resulting copolymer, decreases its tendency to stretch, (i. e. increases its modulus of elasticity), increases its strength and decreases its tendency to change in physical properties with change in temperature. Suitable cross-linking agents for use in this manner include the allyl, methallyl and crotyl esters of succinic, maleic, fumaric, adipic, sebacic, phthalic, acrylic, methacrylic, crotonic and cinnamic acids, glycol diacrylate and dimethacrylate, divinyl ether, tung oil and di- or polyfunctional esters made from maleic or fumaric acid with ethylene

glycol or other polyhydric alcohol and a monohydric alcohol, such as diamyl ethylene dimaleate.

If desired, small amounts of other vinyl and butadiene compounds may be included in these copolymerizations to modify the properties of the copolymers. Polymerizable compounds of interest in this connection include isoprene, butadiene, isobutylene, vinyl ethers, vinyl chloride, vinylidene chloride, acrylate and methacrylate esters, acrylonitrile, styrene and methyl vinyl ketone. The use of relatively small amounts of isoprene or butadiene in these copolymerizations is often desirable because the products obtained are vulcanizable.

By "unified paper backing" we mean that the paper is saturated with a material which binds or welds the fibers together so that the backing will not split or the fibers pull loose under the force exerted by the eucohesive pressure-sensitive adhesive coating when the adhesive tape product is unwound from rolls or removed from surfaces to which temporarily applied; that is, a fiber unity is present which prevents the unity of the backing from being destroyed by the pull of the adhesive.

The paper backing may be creped, crimped, embossed, molded or otherwise formed so as to provide rugosities or corrugations whereby stretchability and an interrupted contacting surface are secured in the adhesive sheet product to facilitate unwinding from rolls and removal from stacks or surfaces to which temporarily applied, and to facilitate conforming the adhesive sheet to curved or irregular outlines or surfaces to which it may be applied. For purposes of convenience all such paper will be referred to hereafter as "creped paper." A flat, uncreped paper may likewise be employed where stretchability is not needed or wanted.

Any type of paper or paper-like sheet may be used so long as it is sufficiently porous or bibulous to permit of adequate impregnation to result in the desired unification. It may be made in whole or in part from wood, rope or rag fibers, or from other fibrous material, natural or synthetic, adapted to the making of thin flexible sheet material of adequate porosity and tensile strength after impregnation. Fibrous glass sheets, for example, may be suitably unified with the copolymers of our invention.

The invention is not limited to true paper as the backing. Thus a fabric of carded cotton fibres can be used. Various felted fabrics can be employed. All of these are to be understood as embraced within the term "paper" as used in the claims, distinguishing from woven fabrics.

Impregnation of the porous paper sheet may be by any of the methods well known in the art, for example by knife or roll coating, use of squeeze rolls, dipping, or spraying. Where the paper when wet with water is so weak as to break off readily under tension, we prefer to apply a light preliminary treatment by means of mechanically driven squeeze rolls, followed by careful drying, so as to obtain sufficient wet strength for subsequent handling in a saturating tank or the like. Paper having an initial wet strength, such as may be provided by treatment in the beater with various known materials, may however be used where available; and such paper may be completely saturated in a single treatment as will be more fully described.

In general the paper is impregnated with a total amount of copolymer dry solids approximately equal to the dry weight of the paper, although higher or lower coating weights may be used with certain papers or for special purposes. With the dispersions of this invention it is possible to obtain uniform distribution of the solids within the sheet of paper, and not a mere deposition on the surface of the sheet. This results in a desirably high degree of unification. Before this saturation the paper will be very permeable to air, but after saturation the unified paper will have a greatly reduced permeability such that its porosity value, as hereinafter defined, is at least as high as 200 seconds.

In the following examples, all parts are given as parts by weight.

Example 1

In this example a heavy porous creped paper is impregnated and unified by means of a cross-linked copolymer of one part of vinyl acetate and two parts of 2-ethylbutyl maleate applied in aqueous dispersion. The unified backing is provided with a pressure-sensitive adhesive coating to yield a pressure-sensitive and satisfactorily unified adhesive tape.

The cross-linked copolymer is prepared as follows: 900 parts of water, 9 parts of Duponol ME (technical sodium lauryl sulfate, produced and sold by E. I. du Pont de Nemours & Co., Inc.), 8 parts of polyvinyl alcohol, 9 parts of sodium bicarbonate and 5 parts of ammonium persulfate are charged into a suitable kettle. The reaction mixture is heated with stirring to form a homogeneous solution at 120° F. Then a mixture of 350 parts of 2-ethylbutyl maleate, 115 parts of vinyl acetate and 10 parts of diamyl ethylene dimaleate is added to the reaction mixture. The diamyl ethylene dimaleate is readily prepared by reacting one mole of ethylene glycol with two moles of maleic anhydride and then completing the esterification with amyl alcohol added in excess, and in the presence of a suitable catalyst such as 1% of p-toluenesulfonic acid, followed by distillation to remove excess unreacted amyl alcohol.

The reaction mixture is heated to 150–155° F. to effect polymerization. After 1 hour at this temperature an additional 20 parts of vinyl acetate is added, with a second and third 20 part portion added after 1½ and 2 hours. After an additional hour at this temperature the reaction mixture is heated during a period of 1 hour to 175° F. and is held at this temperature for an additional hour. Thus the total reaction time is 5 hours. At the end of the reaction, 35 parts of 10% sodium bicarbonate solution is added to the reaction mixture. The non-volatile portion of the dispersion amounts to 35–36%. A dried film is found to be strong and flexible.

This dispersion is utilized in unifying a heavy crepe paper, e. g. "Walpole" crepe, produced by the Hollingsworth and Vose Co. of East Walpole, Mass.; an 85 lb. paper (weighing 85 pounds per ream of 480 sheets 24 x 36 inches) and having approximately 5 major crepe lines per lineal inch, an overall caliper of approximately .020 inch, a porosity of 7 seconds, and a lengthwise tensile strength of about 12.5 lbs. per ½ inch, is used. The porosity is determined on a Gurley Densometer, and indicates the numbers of second required for 400 c. c. of air to pass through a 1⅛ inch diameter single thickness of paper under the conditions provided by that instrument.

The paper is first passed through the dispersion to which has been added one-fifth of its

volume of water, and is then passed between squeeze rolls, so as to provide a wet coating weight of 38–40 grains of the dispersion per 24 square inches. The wet paper is then dried in an oven at 120–130° F.; during the first few minutes, the relative humidity in the oven is maintained at 50–75% to permit complete penetration of the dispersed copolymer into the sheet.

After complete drying, the partially treated paper is given a further impregnation with the undiluted dispersion, preferably by a combination of floating on, and dipping through, the dispersion, with the final coating weight again being controlled by means of squeeze rolls. The combination of floating, whereby the dispersion penetrates the sheet and forces out the entrapped air, and dipping, whereby both surfaces of the sheet are well covered with the dispersion, ensures the complete and uniform impregnation of the sheet with the dispersion. Such a method of impregnation is more fully described in U. S. Patent No. 2,227,444, issued January 7, 1941, to R. G. Drew. A wet coating weight of 21–24 grains per 24 square inches is thus obtained; after drying the sheet, it is found to contain a total of 20–25 grains of dry copolymer, and to have a porosity of at least 1000 seconds.

To secure efficient bonding of the pressure-sensitive adhesive to this unified backing, it is found desirable to prime the surface of the sheet. A suitable primer may be made as follows: 63 parts of zinc oxide is milled into 100 parts of light carcass reclaim (such as No. 34 Reclaim Rubber, from Philadelphia Rubber Works Co. of Akron, Ohio, which is a light carcass grey reclaim containing 62% rubber content and having a specific gravity of 1.20), using the customary roller mill employed in the milling of rubber. Separately, 195 parts of zinc resinate (such as "Pale Zitro" resin, a resinate containing 4.8% combined zinc, obtained from Newport Industries, Inc.) is blended with 49 parts of heavy paraffin oil by heating at 400° F. Three hundred twenty six parts of the milled base, 224 parts of the resin-oil blend, and 44.5 parts of pale gum rosin (such as "Nelio N" pale gum rosin from the Glidden Co.) are then mixed in a heavy duty internal mixer of the Werner-Pfleiderer type. A total of 22 parts of a 50% solution of potassium hydroxide, 33 parts of a 25% solution of casein in ammonia water, and 270 parts of water are added, according to known procedures, so as to produce a smooth, uniform dispersion of the rubber-resin-oil mixture in aqueous vehicle. A coating weight of the primer dispersion of 3–4 grains per 24 square inches is then applied by means of a roll coater to one surface of the unified backing, and is suitably dried, to provide an improved bond between the backing and the subsequently applied pressure-sensitive adhesive.

The same light carcass reclaim used in the preparation of the primer may also be used in making the adhesive. To 198.5 parts of the reclaim is first added, by milling, 1.5 parts of a suitable antioxidant (such as "Flectol H", a condensation product of acetone and amiline produced by the Rubber Service Laboratories Division of Monsanto Chemical Co.). Twelve hundred parts of this mill base is then dispersed, together with 142.5 parts of "Nelio N" rosin and 11.4 parts of heavy paraffin oil, in a mixture of 178 parts of ethyl alcohol and 1780 parts of heptane, to form a smooth fluid mass which is subsequently coated, as by means of a suitable knife coater, on the primed unified backing. Approximately 20–21 grains of the dry adhesive residue per 24 square inches is a satisfactory coating weight. Drying is conveniently accomplished by passing the coated sheet through an oven.

The final product may be slit into tape form and wound on its own backing in roll form. The rolls may then subsequently be unwound without danger of lamination or fuzzing of the treated paper backing. The tape is resistant to the action of moisture, organic solvents, and the like; and the adhesive is not softened nor weakened by prolonged contact with the backing.

Example 2

While the copolymer described under Example 1 may be used for the unification of various other papers, where lighter weight papers are to be treated for use in Masking tape and the like it is preferred to use the somewhat stronger copolymer hereinafter to be described. This polymer is made as follows:

Twenty four parts of Duponol ME, 14 parts of ammonium persulfate and 35 parts of a 28% sodium acrylate solution are dissolved in 2400 parts of water in a suitable reaction vessel. Seven hundred parts of vinyl acetate and 700 parts of 2-butoxyethyl maleate are added and the pH is adjusted to 5.4. The temperature of the agitated reaction mixture is then raised to 60° C. and is kept between 60 and 70° C. for six hours to complete the polymerization and is then cooled. The pH of about 5.3 is raised to 6.8 by the addition of approximately 150 parts of 10% aqueous sodium bicarbonate solution. The product contains 34% of non-volatile material.

A light weight porous crepe paper, such as "Duracel" crepe having a ream weight of 27 lbs. and a porosity of 3 seconds, is impregnated and unified with the copolymer thus obtained, by methods described under Example 1. In this case, the first treatment, using squeeze rolls, provides sufficient "wet strength" so that the partially treated paper is subsequently able to resist the tension of the machine during the floating and dipping operation without breaking or pulling apart. Where necessary, a further saturation of the sheet may be applied after the float and dip, in order to provide a final dry coating weight of copolymer approximately equal to the original dry weight of the paper, i. e. 10–11 grains per 24 sq. in.

The unified backing thus obtained is primed on both sides with a light coating of the primer described in Example 1. One side is then further coated with a light but essentially continuous coating of shellac, applied as a 35 percent solution in alcohol by means of coating rolls; the resulting dried film of shellac is found to be well bonded to the backing by virtue of the intercalated layer of primer, which also aids in preventing penetration of the shellac through the backing and to the face side where it might subsequently prevent adequate bonding of the pressure-sensitive adhesive to the backing.

The pressure-sensitive adhesive of Example 1 may also be used with the backing of the present example, being coated by means of a knife coater or other suitable means on the primed face side of the unified backing. After final drying, the product may be slit and wound into rolls, and makes a highly satisfactory pressure-sensitive adhesive masking tape.

In the above construction, the shellac coating provides a surface to which the adhesive coating does not readily adhere, and therefore permits easy unwinding of the tape from rolls.

However, where the tape is used in multiple layers, as in masking, the shellac provides sufficient anchorage for the adhesive of the next tape layer so that the tape is enabled to remain in position under such light stresses as are occasioned by the action of a lacquer spray gun. Adhesion of the particular adhesive herein described to the original unified backing of this example prior to priming and shellacking is sometimes so light as to cause trouble with the tape lifting or blowing off under these conditions.

The tape of this example is not affected by changes in atmospheric humidity, and is resistant to the solvent and softening action of the usual lacquer solvents. The adhesive retains its full strength even on long contact with the backing.

Example 3

The copolymer of this example is prepared from equal parts of vinyl acetate and 2-ethoxyethyl maleate, with a small proportion of cross-linking agent. It is prepared in aqueous dispersion as follows:

In a reaction vessel equipped with a mechanical stirrer, a thermometer and a condenser, 16 parts of Duponol ME, 12 parts of ammonium persulfate and 45 parts of 28% sodium acrylate solution are dissolved in 1650 parts of water. Nine hundred parts of vinyl acetate, 900 parts of 2-ethoxyethyl maleate and 36 parts of diamyl ethylene dimaleate are added and the pH of the reaction mixture is adjusted to 4.0. The reaction mixture is heated to 65° C., is held at 65 and 70° C. for five hours to effect polymerization and is then cooled. The mixture, which at this point has a pH of 4.6 is raised to a pH of 6.3 by the addition of approximately 150 parts of 10% aqueous sodium bicarbonate solution. The product contains 48% of non-volatile material.

This dispersion is well suited for impregnation of bibulous paper because of its high degree of stability to mechanical action, its small particle size and its high solids content. For example a 27 pound bibulous crepe paper, containing 1% by weight of a melamine-formaldehyde resin to give the paper a high wet strength, may be readily unified and given a high porosity value by saturating with this dispersion in a single "float and dip" operation and then drying.

Such treated paper may be readily converted into tape by applying a shellac backsize from alcohol solution, heating at 125° C. for one hour to improve the unification of the backsized backing and then applying a reclaim adhesive, such as the adhesive of the previous example, to the face side. The finished tape may be slit and wound into rolls.

This tape is superior to previously prepared tapes in being resistant to both water and organic lacquer solvents.

Example 4

Vinyl esters other than vinyl acetate may also be used for the preparation of suitable copolymers for impregnating paper to obtain pressure-sensitive adhesive tape backings. In this example a copolymer of vinyl propionate and n-butyl maleate is used.

Two and one-half parts of Duponol ME, 1 part of ammonium persulfate and 5 parts of a 28% sodium acrylate solution are dissolved in 250 parts of water in a suitable reaction vessel. Seventy five parts of vinyl propionate and 25 parts of n-butyl maleate are added and the pH is adjusted to 5.2. Polymerization is effected by heating with stirring to 80–90° C. for four hours. The final pH is raised to 6.8 by the addition of aqueous 10% sodium bicarbonate solution. The resulting dispersion contains about 30% solids.

This dispersion may be used to saturate and unify porous creped paper which in turn may be made into rolls of tape as in Example 2. Such tape possesses very good strength and is superior to previously prepared tapes in being resistant to both water and to lacquer solvents.

While the specific examples given above show only one type of pressure-sensitive eucohesive adhesive, it is to be understood that other adhesives having similar properties may be substituted therefor. Thus, adhesives having a polyisobutylene base, or a base of crude or of synthetic rubber, synthetic resin may be substituted. Similar substitutions may also be made in regard to primers.

Where backsizing materials are required, materials other than shellac or the like may frequently be used to advantage; thus ethyl cellulose applied from solution in a suitable organic solvent may be used.

Having described various embodiments of our invention, for purposes of illustration rather than limitation, what we claim is as follows:

1. A pressure-sensitive adhesive tape having a unified paper backing member comprising a flexible porous paper impregnated and unified by a relatively non-tacky, non-hygroscopic copolymer of vinyl acetate and a neutral ester of an ethylene-alpha, beta-dicarboxylic acid in which at least about half of the carboxylic acid groups are esterified with a saturated beta-alkoxyethanol, said copolymer having a modulus of elasticity between 2½ and 25 megadynes per square centimeter.

2. A pressure-sensitive adhesive tape having a unified paper backing member comprising a flexible porous paper impregnated and unified by a relatively non-tacky, non-hygroscopic copolymer of a vinyl ester and a neutral ester of an ethylene-alpha, beta-dicarboxylic acid having a modulus of elasticity between 2½ and 25 megadynes per square centimeter.

3. A pressure-sensitive adhesive tape having a unified paper backing member comprising a flexible porous paper impregnated and unified by a relatively non-tacky, non-hygroscopic copolymer of a vinyl ester and a neutral ester of an ethylene-alpha, beta-dicarboxylic acid having a modulus of elasticity between 4 and 15 megadynes per square centimeter.

4. A pressure-sensitive adhesive tape having a unified paper backing member comprising a flexible porous paper impregnated and unified by a relatively non-tacky, non-hygroscopic copolymer of a vinyl ester and a neutral ester of an ethylene-alpha, beta-dicarboxylic acid in which at least about half of the carboxylic acid groups are esterified with a saturated beta-alkoxyethanol, said copolymer having a modulus of elasticity between 2½ and 25 megadynes per square centimeter.

5. A pressure-sensitive adhesive tape having a unified paper backing member comprising a flexible porous paper impregnated and unified by a relatively non-tacky, non-hygroscopic copolymer of vinyl acetate and the di-betaalkoxyethyl ester of an ethylene-alpha, beta-dicarboxylic acid having the formula HOOC—CH=CH—COOH, said copolymer having a modulus of elasticity between 2½ and 25 megadynes per square centimeter.

6. A pressure-sensitive adhesive tape having a

unified paper backing member comprising a flexible porous paper impregnated and unified by a relatively non-tacky, non-hygroscopic copolymer of vinyl acetate and 2-butoxyethyl maleate, said copolymer having a modulus of elasticity between 2½ and 25 megadynes per square centimeter.

7. A pressure-sensitive adhesive tape having a unified paper backing member comprising a flexible porous paper impregnated and unified by a relatively non-tacky, non-hygroscopic copolymer of vinyl acetate and 2-butoxyethyl maleate in approximately equal parts by weight, said copolymer having a modulus of elasticity between 2½ and 25 megadynes per square centimeter.

8. A pressure-sensitive adhesive tape having a backing member comprising a flexible porous paper impregnated and unified with an approximately equal weight of a copolymer of monomers comprising (*a*) a neutral vinyl ester and (*b*) a neutral ester of an ethylene-alpha, beta-dicarboxylic acid, said copolymer having a modulus of elasticity of between 2½ and 25 megadynes per square centimeter.

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PRESSURE SENSITIVE ADHESIVE TAPES

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5 Claims. (Cl. 117—122)

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This invention relates to pressure-sensitive adhesive tapes, and more particularly to the preparation of such tapes wherein the adhesive thereof comprises a polyvinyl pressure-sensitive adhesive, and wherein the backing may be a transparent, non-fibrous sheet material such as regenerated cellulose.

An accepted backing material for transparent pressure-sensitive adhesive tapes is regenerated cellulose. Because of its smooth, non-fibrous, glossy surface, commercially satisfactory regenerated cellulose adhesive tapes have included a priming coat for the purpose of improving the bond between the pressure-sensitive adhesive and the backing by creating a preferential affinity of the adhesive for the surface of the primed backing to which it is applied, compared with its affinity for the surface of the backing without the interposition of the priming coat, and thus permit, after the tape has been wound upon itself in roll form, successful unrolling thereof without destructive separation or delamination of the adhesive from the backing. Rubber-resin adhesives generally used as pressure-sensitive adhesives in such tapes do not have commercially sufficient adhesion, when applied directly to the smooth glossy surface of regenerated cellulose in the absence of a priming coat or of some special technique of application, to permit such satisfactory unrolling.

This application is concerned with the preparation of non-rubber polyvinyl resin pressure-sensitive adhesives which may be directly affixed as firmly adherent coatings to regenerated cellulose or other similar smooth-surfaced transparent sheet backings and is a continuation-in-part of my application Serial No. 349,973, filed August 2, 1940, now Patent No. 2,426,257.

The foregoing application discloses inter alia the preparation of pressure-sensitive adhesives formed of a polyvinyl ester, a resin compatible with the polyvinyl ester, and a non-volatile liquid plasticizer compatible with both the polyvinyl ester and the resin; and wherein the polyvinyl ester serves as the film-forming vehicle for the adhesive and is present in sufficient proportion to impart structural supporting characteristics which permit the formation of a relatively thin continuous cohesive flexible coating thereof on a flexible sheet backing, inclusive of regenerated cellulose, to form a pressure-sensitive adhesive tape.

In so far as tapes having regenerated cellulose backings are concerned, such an adhesive has been found to have a remarkable affinity for the

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regenerated cellulose surface to which it has been applied when the adhesive is prepared in accordance with the following formula:

	Parts
Vinyl co-polymer VYHH	30
Nevillac resin	30
Santicizer B16 (butyl phthalyl butyl glycollate	42

The vinyl co-polymer is a standard polyvinyl resin of the acetate-chloride type and in the form which has been used for the adhesives hereof has a chloride content of about 87% and a molecular weight of about 9,500–10,500. It is a product of Carbide & Carbon Chemicals Corporation. It constitutes the film-forming vehicle and is responsible for the elastic and cohesive characteristics of the adhesive.

The Nevillac resin is a phenol-modified coumarone-indene resin, a product of Neville Company, and is used in the above formula, has a melting point in about the range of 85 to 95° C. It forms the adhesive constituent of the adhesive.

Santicizer B16 is one of the Monsanto Chemical Company's non-volatile liquid plasticizers which are alkyl phthalyl alkyl glycollates. This particular Santicizer B16 is butyl phthalyl butyl glycollate. It activates the Nevillac resin to stickiness and renders the adhesive coating as a whole flexible.

These three ingredients may be added to a common organic solvent, such as ethyl acetate or acetone, in the order of plasticizer, co-polymer and Nevillac. The solvent can then be driven off as necessary to a point where the solids content is suitable for spreading as by a doctor blade or roll on regenerated cellulose sheet material—for example to about 50 to 80%, preferably 75%. Both the mixing and spreading may be accomplished at room temperature, but artificial drying may be helpful in driving off the solvents after the solution is spread upon the backing. It has been found that the tack of the coating improves as the thickness increases from .002" to .005". Hence the thicker coat is desirable.

A regenerated cellulose sheet, thus directly coated with my transparent adhesive in a one-coat operation without any interposed primer coat, may be slit and rolled and will meet the commercial requirements for a transparent cellophane pressure-sensitive adhesive tape. The roll may be unwound without delamination of the adhesive onto the backing even in the absence of separate interliners, and the tape can, like the usual cellophane tapes, be re-used. The adhe-

sive, which is clear and transparent, ages well and has good adhesion to metal, wood, paper and other materials to which cellophane tapes are now generally applied. The adhesion to skin is, however, not as aggressive as that of rubber-resin pressure-sensitive adhesives. This particular quality has been found to be a decided advantage because the tape is thus less sticky and less annoying to handle.

The proportions and ingredients so far recited represent the best formula with Hard Nevillac resin (i. e. 85–95° C. melting point) for general regenerated cellulose use. It should be noted that the film-forming ingredient and adhesive resin constituent are in a 1 to 1 ratio. Variation of this ratio is permissible, but experience shows that variation has resulted in sacrifice in quality, particularly with regard to the affinity for the regenerated cellulose. A decrease in vinyl polymer content, so that the ratio is 20–40–42, instead of 30–30–42, will result in a decrease in the adhesion and cohesion characteristics, but will increase the tack. On the other hand, if the plasticizer content be independently varied within the limits of from 90 to 50% of the combined vinyl polymer-resin base, the adhesion and cohesion will increase with decrease of plasticizer content, but the tack will decrease. In our experience, the 1 to 1 ratio provides the most desirable qualities of adhesion and cohesion for the purposes of a regenerated cellulose tape, and the tack can be kept suitably high with this ratio by the use of a higher proportion, e. g., 70% of plasticizer, aided, if desired, by a coating thickness of about .005". In any event, the film-forming vehicle content must be sufficiently high to give adequate cohesive strength to the adhesive coat, and, in accordance with this invention, must exceed 12% of the total content.

Equally successful results have been secured with the use of softer Nevillac resins, which range down to a melting point of about 65° C. These softer resins are also phenol modified coumarone-indene resins. Use of such softer resin permits a reduction in the plasticizer content, and, from the standpoint of cost and lighter color, an adhesive having the following formula is even more desirable than one following the Hard Nevillac formula:

	Parts
Vinyl co-polymer VYHH	30
Soft Nevillac resin	30
Santicizer B16 (butyl phthalyl butyl glycollate)	36

It will be noted that here the plasticizer content is in the ratio of .6 to the combined vinyl co-polymer and Nevillac content. Generally this plasticizer ratio may be .1 part less (figured on the combined co-polymer resin content) than in the case of the Hard Nevillac formula where, as above given, the ratio is .7. However, additional plasticizer variation will produce corresponding variation in tack, adhesion and cohesion results, generally corresponding to those heretofore discussed in the case of the Hard Nevillac.

In tapes constructed in accordance with this invention the adhesion of the tape mass to other regenerated cellulose surfaces may be in the range of from 0.6 to 1.2 or more pounds and the mass coating exhibits substantially the same degree of adhesion to its regenerated cellulose backing as it does to an external regenerated cellulose surface.

For the purposes of determining "adhesion" to external surfaces, as referred to in the preceding paragraph, a one-inch wide strip of convenient length of the tape to be tested is placed tacky surface down upon a smooth surfaced Bakelite panel under temperature conditions of 70° F. The panel is then placed at a 15° inclined position and a seven-pound roller which is free to move vertically is passed over the strip at the rate of one foot per minute up and back to adhere the pressure-sensitive surface to the panel. One end of the strip is then attached to the clamp of a tensile strength Scott tester and the average number of pounds required to pull a substantial length of the tape off the Bakelite surface at an approximate 180° angle and at a rate of one foot per minute is determined.

For the purposes of determining adhesion of a coating to its own backing, a double-face adhesive strip is interposed between the Bakelite panel and the strip to be tested. Such a double-face adhesive tape may be an ordinary surgical tape coated on both sides. The regenerated cellulose tape to be tested is then separated at one end of the tape from the adhesive mass and the clamp of the tester is affixed to this backing alone, the tester stripping the regenerated cellulose backing from its own mass which remains adherent to the double-face tape.

In addition to adhesion characteristics of the above type, it has been found that the mass film has extensive stretchability and a tensile strength in a one-inch width of about ¾ pound at 70° F. These latter characteristics, taken in connection with the adhesion characteristics, are factors contributing to the production of a tape which does not delaminate upon unrolling.

Cohesion of the above referred to masses are shown to be such that they have a "creep" characteristic exceeding 20 minutes as determined by placing a one-inch strip of the tape of several inches length, tacky side down, over a horizontally disposed, raised, one-inch diameter Bakelite cylinder, and suspending a one-pound weight from each end of the tape. The apparatus is then placed in an oven at 105° F. for a period of 15 minutes, after which time the tape is slashed across the top of the cylinder and the time required for either portion of the tape to fall from the cylinder is an arbitrary value assigned to the tape as its "creep" value. Some tapes of this invention reach a creep value exceeding 100 minutes.

A further determinative characteristic of adhesive tapes is that of aging. Tapes of this invention have successfully withstood a standard accelerated aging test comprising storage of the tape under 300 lbs. oxygen pressure at 105° F. for a period of one week. After such storage the tapes are still tacky and having adhesion values, determined in accordance with the previously given test, in excess of 0.6 lb., they can still be unrolled without delamination and instances of similar behavior have occurred even when the period in the oxygen bomb is as much as 3 weeks.

A further desirable feature is found in these tapes in that they exhibit a definite stability over a range of temperature and can be unwound without any detrimental delamination of the adhesive at any temperature in ranges as wide as from 40 to 160° F.

The Monsanto Chemical Company produces "Santolite" resins which may be successfully used instead of Nevillac resins. These Santolite resins are aryl sulphonamide-formaldehyde resins. Santolite MHP, preferred because of its

light color, has a melting point of about 65° C. and therefore its action is more similar to that of the soft Nevillac resin and should be used in the proportion of the soft Nevillac resin. Santolite MS, being a still softer resin (melting point 50° C.) detracts somewhat from the cohesion and requires a still further reduction in plasticizer with the plasticizer content, in some cases, being as low as 30% of the combined co-polymer resin content. However, it is contemplated that adhesives of this invention may be applied to suitable backings by a calendering operation rather than by a solvent spread as hereinbefore described. Thus the ingredients may be mixed and brought to the proper consistency for spreading by transferring the mix to a hot rubber mill to dissolve the solvent; or in some cases of relatively high resin-plasticizer content (for instance, 2 parts of co-polymer to 3 parts of resin and 3 parts of plasticizer), the co-polymer may be dissolved directly in a hot (140–150° C.) mixture of the resin and plasticizer and calendered at that or a lower temperature.

With regard to the film-forming vehicle, the superior results accomplished on cellophane with the co-polymer have not been attained with other polyvinyl esters, although polyvinyl acetate will be found acceptable especially when a smooth-surfaced backing is not contemplated or when priming coats are permissible. In general, polyvinyl acetate has softer characteristics than that of the co-polymer and therefore imparts less cohesive strength to an adhesive, while polyvinyl chloride has limited solubilities, a characteristic which renders solvent operations difficult.

In the case of polyvinyl acetate, pure phenolic resins (Beckacite) may be satisfactorily used as well as Nevillac. The Beckacite resins are not compatible with the co-polymer.

As to the plasticizer, modifications can be made so long as compatibility in the proportions used is observed. Other satisfactory plasticizers for the Nevillac-co-polymer mix, though not preferred, are other non-volatile liquid esters of phthalic acid, including either the dialkyl phthalates — dibutyl phthalate and dicapryl phthalate—or other mixed esters of phthalic acid and alcohols or hydroxy acids, dibutyl sebacate and mixed aryl sulfonamides, such as Santicizer 8 (Monsanto Chemical Co.). Either dibutyl phthalate or Santicizer B16 are compatible with polyvinyl acetate-phenolic resin mixes.

Adhesives may be suitably formulated in accordance with this invention for application to other sheet backings, either of the non-fibrous or fibrous variety, including woven or unwoven fibrous backings and smooth surfaced backings of the type of cellulose acetate, ethyl cellulose, polyvinyl ether, rubber hydrochloride or polyamides such as sheet nylon.

I claim:

1. A pressure-sensitive adhesive tape, comprising a flexible smooth-surfaced non-fibrous sheet backing material having affixed directly thereto on one side a firmly adherent coating of a normally tacky pressure-sensitive adhesive, whereby said tape may be rolled upon itself and unrolled without destructive delamination of the tape, said adhesive consisting essentially of a polyvinyl acetate-chloride co-polymer film-forming vehicle and a compatible normally solid meltable phenol modified coumarone-indene resin in about equal proportions, and a non-volatile liquid alkyl phthalyl alkyl glycollate plasticizer compatible with both said co-polymer and said resin in the proportion of about 30–90% of the combined weight of said co-polymer and resin.

2. A pressure-sensitive adhesive tape comprising a flexible smooth-surfaced non-fibrous sheet backing material having affixed directly thereto on one side a firmly adherent coating of a normally tacky pressure-sensitive adhesive, whereby said tape may be rolled upon itself and unrolled without destructive delamination of the tape, said adhesive consisting essentially of a polyvinyl acetate-chloride co-polymer film-forming vehicle and a compatible normally solid phenol modified coumarone-indene resin, said co-polymer and said resin being in about equal proportions, and a non-volatile liquid plasticizer compatible with both said co-polymer and said resin in the proportion of about 30–90% of the combined co-polymer resin weight.

3. A pressure-sensitive adhesive tape comprising a flexible smooth-surfaced non-fibrous sheet backing material having affixed directly thereto on one side a coating of a normally tacky pressure-sensitive adhesive, said adhesive being formed of a polyvinyl acetate-chloride co-polymer film-forming vehicle, phenol modified coumarone-indene resin and a non-volatile liquid plasticizer compatible with both said polymer and said resin, the proportion of ingredients being about 20–30 parts of co-polymer, about 30–40 parts resin and about 36–42 parts plasticizer.

4. A pressure-sensitive adhesive tape as claimed in claim 3 wherein the plasticizer is an alkyl phthalyl alkyl glycollate.

5. A pressure-sensitive adhesive tape as claimed in claim 3 wherein the plasticizer is butyl phthalyl butyl glycollate.

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INSULATING TAPE

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Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

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This invention relates to the insulation and protection of electrical conductors, and to insulating tape employed therein.

Synthetic polymeric materials have recently replaced rubber and guttapercha to a great extent in the insulation of wires and cables, particularly those exposed to outdoor conditions or to oils or solvents. Materials such as polyvinyl chloride and polymers of ethylene, for example, have been applied by extrusion methods to copper wires to provide insulated conductors having excellent electrical characteristics as well as good chemical and mechanical properties. Such insulated wire has been widely accepted as an improved product.

The advantages of such insulation are not fully realized, however, when splices between lengths of the wire must be covered with previously known classes of insulation. The commonly used unvulcanized rubber base electrician's tape, for example, is not resistant to oils or sunlight, and does not adhere well to the synthetic polymer insulation. The tape is also low in mechanical strength, and a bulky outer wrapping of friction tape is ordinarily required to provide compression and mechanical protection.

As an alternative to the use of rubber insulating tape, strips of polymer of the same formula as that on the insulated wire have sometimes been used. In such an application, heating and molding are necessary in order to weld the polymer together into an integral insulating layer. The process is inconvenient and time-consuming, and requires special apparatus.

The present invention provides, for the first time, means for permanently covering, insulating, and mechanically protecting splices in polymer-covered wires as just described, by simple hand application of a single strip of stable, stretchable, retractable, pressure-sensitive adhesive tape. Our novel tape also has many additional uses, as hereinafter suggested.

Attempts have previously been made to provide similar strips, or films, of polymer with adhesive coatings so as to avoid the necessity of the subsequent heating and molding operations in covering and insulating wire splices. For example, polyvinyl chloride plasticized with not more than 20 parts of the usual plasticizer such as tricresyl phosphate or dioctyl phthalate has been sheeted out in roll form in thicknesses up to 4 mils or greater, and coated with a specific pressure-sensitive adhesive consisting of rubber, polyisobutylene, and a resinous material, in an attempt to produce a transparent flexible adhesive tape or sheet. With this amount of plasticizer, however, the sheet is found to be quite stiff and rigid. Very high stress is required to obtain any appreciable elongation; for example, a strip one inch in width and .004 inch in thickness of a mixture of 100 parts of an 89:11 vinyl chloride-vinyl acetate copolymer and 20 parts of dioctyl phthalate required a stress of 30 lbs. to produce even as little as 10% elongation. Increased elongation results in a whitening of the film, and the stretched film will then no longer retract to its original length at room temperature. Films, or coated adhesive tapes, having these properties cannot readily be applied by hand to wire splices or the like. While thinner films of similar composition might conceivably be used because of their reduced strength per unit of width, the low elasticity still precludes the acceptance of such tapes for applications such as the covering of wire splices. In addition, thicknesses of at least about four mils, and even up to twelve mils or somewhat higher, are generally preferred by electricians because of the reduced number of turns required for adequate insulation, as well as the absence of the flimsiness characteristic of thinner films.

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Films have also been prepared with increased amounts of dioctyl phthalate or the like in an attempt to reduce the stress requirements and improve the elasticity. Thus, a composition consisting of 100 parts of a vinyl chloride polymer and 33 parts of dioctyl phthalate was calendered to a thickness of four mils and coated with a pressure-sensitive adhesive as hereinabove described. While the physical properties of the film were much improved, it was found that this particular adhesive as well as various other pressure-sensitive adhesives rapidly became soft and "pasty" when in contact with this or other vinyl polymer films containing more than about 20 parts of liquid type plasticizers. The resulting tape, when wound under tension around a splice or bundle of wires, soon loosened and became ineffective. This tendency was increased with even slight increase in temperature above normal room temperature.

The present invention avoids these and other defects of previously known insulating and binding materials of the type described, and provides, among other things, an improved insulated spliced electrical conductor which is electrically, mechanically and chemically effective, and which may be readily and quickly prepared without the use of special procedures or equipment. These unique and valuable results are obtained

by utilizing an insulating tape in the form of a relatively thick but easily stretchable and highly elastic pressure-sensitive adhesive tape comprising a well-bonded, water-insoluble, non-corrosive, normally tacky and pressure-sensitive adhesive coating on a plasticized vinyl chloride polymer film which is in permanent equilibrium with the adhesive. By "permanent equilibrium" it is meant that the pressure-sensitive adhesive layer neither softens (becomes "pasty") nor loses tackiness (becomes non-adherent) on prolonged contact with the backing or film layer. The adhesive remains aggressively tacky, and also remains "eucohesive" (by which it is meant that it is more cohesive than adhesive such that offsetting or transfer of adhesive material does not result when the tape is unwound from rolls or removed from surfaces to which temporarily applied and can be handled without transfer of adhesive material to the fingers).

In order to secure permanent equilibrium between backing and adhesive, we employ with the vinyl chloride polymer a combination of modifiers including a substantial but minor amount (not to exceed about 20 parts per 100 parts of the vinyl polymer) of a low molecular weight liquid plasticizer such as dioctyl phthalate, together with a substantially equal or somewhat greater amount of a high molecular weight resinous type plasticizer, the amount of the latter in any event being sufficient, together with the liquid plasticizer, to provide the desired degree of stretch in the final film. "Paraplex G–25" is a preferred example of a suitable resinous type plasticizer. It is sold by Resinous Products & Chemicals Corp., and is a soft, viscous alkyd resin having a specific gravity of 1.06, and an acid number of not more than 2.0; it is soluble in esters, ketones, aromatic and chlorinated hydrocarbons. Another high-molecular-weight plasticizer material which has been found useful in providing suitably stretchable and elastic vinyl polymer films is polymerized ethyl acrylate. Another example is polymerized vinyl butyl ether.

While resinous or high molecular weight modifiers such as "Paraplex G–25" are themselves capable of producing the desired degree of strength, stretch and elasticity in vinyl chloride polymer films, and furthermore are generally classed as "non-migrating" or "permanent" type modifiers or plasticisers, it is surprisingly found that these materials do not provide for permanent equilibrium of adhesive and backing as herein defined. Instead, it has been shown that pressure-sensitive adhesives in prolonged contact with highly stretchable and elastic films consisting solely of vinyl polymer and resinous modifier lose a great deal, if not all, of their initial tackiness or pressure-sensitivity. When tape made in this way is unwound from roll form, after a moderate period of storage, and applied to a splice, it does not adhere either to the electrical conductor or to its own backing, and hence is of no value as an insulating and protective coating.

The present invention provides an electrical insulating tape having properties of stretch and elasticity which render it highly effective for wrapping wire and cable splices. The tape is stretchable to the extent of at least about 50% at room temperature as measured in a tensile tester (such as a Serigraph Model I–P–4, manufactured by the Henry L. Scott Co. of Providence, R. I.). The tape can be readily stretched to this extent by pulling between the hands. In fact, the invention provides tapes which are

stretchable to the extent of at least about 100%, which is preferred. The elasticity of the tape is a valuable feature in making possible snug wrappings and coverings. The present tape is highly elastic as shown by the fact that when a strip is elongated 30% at room temperature and then released it will retract at room temperature to substantially the original length. The invention provides tapes that will substantially completely retract when elongated as much as 50% or even more. The method employed for making such retraction tests of elasticity is as follows. A number of tape lengths are cut. Each length is suspended from an upper clamp and is provided with a light clamp (weighing about 10 grams) at the lower end to provide means for applying a weight. Each tape strip is 1 inch wide and 5 inches long between clamps. Weights of various amounts are applied to the different samples to determine what weight is needed to produce the desired elongation (30%, for example) in 15 seconds. In the case of this sample, the weight is promptly removed at the end of the 15 seconds, and the length of the tape between clamps is measured at different time intervals to determine the retraction. The weight of the lower clamp is relatively so minute that it does not affect the result.

The preferred thickness of the backing film for the electrical tape is 4 to 20 mils. A thickness of about 5 to 10 mils is generally most useful.

The values of caliper, stretchability, flexibility, elasticity, adhesion, electrical properties, chemical stability or inertness, solubility, and other properties of the insulating tapes are designed and selected for greatest utility in the wrapping and protecting of splices in synthetic polymer insulated copper wire, as previously indicated. Some or all of these properties render the product useful for other purposes. For example, the adhesive tape may be used to bind together a number of insulated electrical conductors into a permanently compact, flexible, oil-resistant bundle or harness, by spirally winding such a bundle with a single overlapping strip of the tape applied under considerable tension. A similar spiral winding on metal racks employed in electroplating operations provides a chemically resistant coating which remains firmly attached to the rack during immersion in the plating bath. Single thicknesses of the tape are useful as abrasion or wear-resistant adherent surface coatings on flat or curved surfaces.

The following examples of insulating tapes in the form of pressure-sensitive adhesive tapes having a vinyl polymer film base were prepared with a vinyl chloride-vinyl acetate copolymer softening at about 280° F. and in which the ratio of vinyl chloride to vinyl acetate was approximately 89:11. The commercially available "Vinylite VYNS," sold by Carbide and Carbon Chemical Corp., is a suitable copolymer corresponding to this description. Other equivalent materials include copolymers having other vinyl chloride-vinyl acetate monomer ratios, such as 95:5. Polyvinyl chloride itself is satisfactory in many formulations, as are many of the copolymers of vinyl chloride and vinylidene chloride, of which one example is "Geon 200–X–6," a vinyl chloride-vinylidene chloride copolymer having a softening temperature of about 260° F., sold by B. F. Goodrich Co. Polymers softening at 300° F. or higher are ordinarily to be preferred where extremely high heat resistance solvent resistance, and the like are essential.

Many liquid plasticizers other than the dioctyl phthalate of the various examples may be substituted therefor. The plasticizer must be compatible with the vinyl polymer, and must be sufficiently low in volatility so that it is not driven off during milling and calendering, or during subsequent storage and use. Tricresyl phosphate, dibutyl phthalates, and butyl phthalyl butyl glycollate, for example, appear to be equally effective in most of the compositions herein described. All of these compounds are capable of producing pastiness in water-insoluble pressure-sensitive adhesives coated on vinyl backings when used in proportions greater than about 20 parts per 100 parts of the vinyl polymer.

Likewise, various compatible non-migrating resinous or high molecular weight modifying materials having a plasticizing effect on the vinyl polymer employed may be substituted in whole or in part for the specific alkyd resin hereinbefore mentioned. Ethyl acrylate polymer has been found useful, as previously noted; this modifier has somewhat less tendency to cause tack loss than does the "Paraplex G–25," hence may be used in even greater amounts in many formulations. A resinous material having properties essentially equivalent to Paraplex G–25 for our purposes has been prepared by heating together sebacic acid, propylene glycol, and ethylene glycol in a 10:9:1 molar ratio to a low acid number.

It will be understood that, where specific ratios of specific polymers, low molecular weight plasticizers, and high molecular weight plasticizers are described in the examples, substitution of equivalent but somewhat different materials may require alteration of these ratios in order to obtain equivalent results, all in conformity with well-recognized principles.

Various modifying agents which impart specific properties to the film may be added if desired. For example, a small amount of calcium stearate added prior to milling and calendering acts as a stabilizer in preventing darkening of the vinyl polymer or of the film. Other examples are lead silicate, calcium silicate, and triethanolamine.

In general, the tape products herein described are most conveniently and economically prepared by a series of steps including pre-mixing, milling, and calendering the vinyl polymer-plasticizer mixture into continuous film form, temporarily attaching the film to a carrier belt or web, coating the exposed surface of the film with an adhesive primer and subsequently with a pressure-sensitive adhesive, removing the coated film from the carrier, slitting into narrow widths, and winding the resulting adhesive tape into roll form on suitable cores. In place of calendering, other means may be employed for forming the film. Deposition from solution in a suitable volatile liquid vehicle, followed by heating to remove the vehicle and, where necessary, to homogenize the film, has some advantages, particularly in the case of the thinner films. However, the action of the calender or similar devices seems to impart some additional and desirable properties to the resulting film, particularly with respect to stretchiness and elasticity, and such methods are generally to be preferred.

Where a varnished cambric or Holland cloth carrier belt is used, sufficient adhesion of film to belt may be obtained simply by combining the two on the bottom roll of the calender under a light pressure and with the roll at a temperature of the order of 110° F. A heavy paper web with a light weight surface coating of a low tack pressure-sensitive adhesive may economically replace the varnished cambric. In any event, the carrier web is simply an aid to the successful commercial coating of the highly stretchable film, and may be dispensed with where other suitable methods of handling this type of material are available.

Primer and adhesive compositions are preferably, but not necessarily, applied from solution or suspension in a volatile liquid vehicle, as shown in the examples. The volatile vehicle is removed after each coating operation, preferably by evaporation at elevated temperatures.

Example 1

A mixture of 700 parts by weight of "Vinylite VYNS," 200 parts of "Paraplex G–25," 100 parts of dioctyl phthalate and 25 parts calcium stearate was milled together on a rubber mill, previously heated to 250° F., until homogeneous, and was then calendered to a thickness of 4 mils. The resulting transparent film was lightly bonded to a varnished cambric carrier web, and was then primed, after which it was coated with a pressure-sensitive adhesive. The primer was made by mixing 985 lbs. of an ammoniacal casein solution containing 80 lbs. of casein with 624 lbs. of an aqueous dispersion containing 38% by weight of a coplymer of 50 parts butadiene and 50 parts styrene. The primer coating was dried to remove the water, resulting in an extremely thin primer film. The formula of the pressure-sensitive adhesive was as follows:

	Parts by weight
Rubbery butadiene-styrene copolymer	100
Zinc oxide	5
Titanium dioxide	10
Yellow pigment	0.3
Oil-soluble heat-reactive phenol-aldehyde resin	12
Ester gum	40
Paraffin oil	25
Soft coumarone-indene resin	40
Heptane	300
Alcohol	About 10

In compounding the adhesive, the copolymer and pigments were first milled together. The mill base was then blended with the ester gum, paraffin oil, coumarone-idene resin, and finally with the phenol-aldehyde resin in a heated heavy duty internal mixer. After a brief further heating at a higher temperature, the batch was cooled. The heptane was then added in small portions, and sufficient alcohol was finally added to bring the viscosity to the proper value for coating. The primed film was coated with the adhesive solution, followed by drying to remove the solvent. About 6.5 to 7.5 grains of adhesive, on the dry basis, were applied to 24 square inches of the film.

The coated film was removed from the temporary liner and slit into narrow widths. The resulting tape was highly stretchable and elastic, and provided an excellent insulating and protecting covering when wound around an electrical conductor. On an irregular surface, such as a wire splice, the elasticity or regain was sufficient to provide an extremely compact covering. The tape was found to have at least about 100% stretch, and a tensile strength of about 20 lbs. per inch width.

Strips of the tape were stretched to 20% and to 50% elongation, and were then allowed to re-

tract under no load. The strips returned to their initial length in 15 to 30 minutes and in 12 hours, respectively.

An adhesive tape was similarly prepared from a film in which the same polymer, resinous plasticizer, and liquid plasticizer were in the relative proportion of 100:29.5:17.6. This film was somewhat softer and more readily stretchable. However, the adhesive coating was in permanent equilibrium with the backing, as shown by the fact that after one year of natural ageing at room temperature the adhesion and firmness values of the pressure-sensitive adhesive coating remained unchanged.

Increasing the plasticizers in the above film to a final formula of 100:30:20 yielded a composition which, in the form of 4 mil film, was found to be somewhat weak. However, this composition produced a reasonably satisfactory backing in thicknesses of about twelve mils. Pressure-sensitive adhesives coated on this backing were found to soften to a very slight extent after prolonged ageing in the final tape rolls, but the tape remained fully satisfactory for such uses as the binding of wire harnesses and the like.

On the other hand, films prepared from the above ingredients in the proportions 100:26.5:6.7, primed, and coated with adhesive, were found to be too tough and inelastic for most uses, even though the adhesive coating remained tacky and in good condition. When such films were elongated to more than approximately ten or twenty per cent of their initial length, they were found to acquire a permanent set and would not then retract to their original length. A slight increase in the proportion of dioctyl phthalate, for example, to about eight or ten parts, improved the films in this respect. On the other hand, adhesives coated on films plasticized with from 40 to 70 parts of "Paraplex G–25" and in the absence of the dioctyl phthalate were soon found to become deficient in tackiness.

Example 2

The plasticized vinyl polymer film of Example 1 was primed with a synthetic rubber-resin primer composition applied from solution in organic solvent, and coated with a natural rubber base pressure-sensitive adhesive. The resulting transparent pressure-sensitive adhesive tape was useful for wrapping splices in electrical conductors and for other purposes. The adhesive and backing were found to be in permanent equilibrium. The transparent nature of the tape was advantageous where it was desirable periodically to inspect the protected surface.

The composition used as the primer in this example consisted of a solution, in a mixture of 100 parts toluol and 20 parts methyl ethyl ketone, of 20 parts of a pure hydrocarbon thermoplastic terpene resin having a melting point of 115° F. and a zero acid number, and 25 parts of a rubbery butadiene-acrylonitrile copolymer.

The transparent pressure-sensitive adhesive was prepared by blending 288 lbs. of latex crepe rubber, 175 lbs. of the thermoplastic terpene resin having a melting point of 115° F., 2.88 lbs. of tetramethyl thiuram disulfide, and 3 lbs. of an antioxidant such as "Flectol H" (a condensation product of acetone and aniline melting at 120° C.), in solution in heptane containing a small amount of denatured alcohol as a viscosity reducing agent.

Example 3

Various pigments and colors may be added both to the backing and to the adhesive formulation of my insulating composition in order to improve the appearance, or to provide a distinctive color, or for other purposes. Heavy pigment loading of the vinyl film for example is found to improve the heat resistance.

A film twelve mils in thickness was prepared from a mixture of 700 parts "Vinylite VYNS," 200 parts "Paraplex G–25," 100 parts dioctyl phthalate, 1100 parts titanium dioxide pigment, and 30 parts calcium stearate, together with 100 parts of a mold inhibiting agent such as "Shirlan Extra" (salicyl anilide). The film was primed with the primer of Example 2 and coated with a polyacrylate base pressure-sensitive adhesive. The adhesive was composed of a copolymer of 75 parts of 2-ethylbutyl acrylate and 25 parts ethyl acrylate, tackified with a thermoplastic terpene resin, and firmed up by heating with small admixed amounts of zinc resinate and an oil soluble heat-reactive phenol-formaldehyde resin. Titanium dioxide was included as a pigment to produce a white adhesive. The produce was cut into narrow widths and wound into roll form, in this case with a varnished cambric interliner.

Samples of the tape showed approximately 100% strength at break, and had a tensile strength at break of approximately 30 lbs. per inch width. Retraction to original length from 20% elongation was complete in somewhat under five minutes, and from 50% elongation in approximately twenty-four hours.

Example 4

To produce a completely flame-resistant tape product, the primed film of Example 3 was coated with a pressure-sensitive adhesive consisting essentially of polymerized chloroprene and chlorinated diphenyl in approximately equal proportions by weight. The adhesive was applied from solution in a high aromatic content hydrocarbon solvent.

Example 5

To the film composition of Example 1 was added five parts of carbon black. The resulting film had a black glossy appearance and considerably increased tensile strength. The elasticity was somewhat reduced, but the film retracted to its original dimension from approximately 50% elongation in somewhat less than twenty-four hours.

The film was primed with the primer of Example 2 and coated with an adhesive consisting of 100 parts of a mixture of equal parts of natural rubber and Buna-S synthetic rubber, 50 parts of zinc oxide, 5 parts of carbon black, and 50 parts of heat treated wood rosin. A small amount of Flectol H antioxidant was also added, and the material was dispersed in heptane to a coatable viscosity. The resulting tape product was particularly applicable to the covering of splices in copper wires carrying an insulating coating of black pigmented plasticized synthetic polymer.

It will be seen that ~~hereinabove~~ we have described various embodiments of our invention for purposes of illustration. The novel article of our invention is a broadly new article of commerce. Prior to our invention there was no electrical or plastic tape available which was similar to the product of this invention either in performance characteristics or in appearance or handling characteristics. No pressure-sensitive adhesive tape was previously available which was of suffi-

cient thickness (i. e., 4 to 20 mils) to provide suitable dielectric strength and yet of handling characteristics such that it was readily stretchable by hand pulling to an extent of at least 50% at room temperature and substantially completely slowly retractable from an elongation of 30% as herein specified. Again, no tape of such thickness and other properties was previously available to industry in which the backing film had high resistance to both hydrocarbon oils and water and also was in "permanent equilibrium" with the pressure-sensitive adhesive coating, so as to avoid pastiness or tack loss of the adhesive. For these and other reasons, the novel article of this invention is a commercially new thing: it is a new type of tape, actually and commercially. There is no product in the prior art which resembled it, or was able to compete with it.

Where the term "rubber resin type" is used in defining the adhesive layer in the claims, it simply means a normally tacky and pressure-sensitive adhesive, such as one having properties of tack, pressure sensitivity, cohesiveness, et cetera, similar to the physical characteristics possessed by rubber resin, pressure-sensitive adhesives of the prior art.

Having described various embodiments of our invention, for purposes of illustration rather than limitation, what we claim is as follows:

1. A pressure-sensitive adhesive insulating tape wound upon itself in roll form and comprised of: a stretchable and elastic film backing having a thickness of 4 to 20 mils and formed of a homogeneous mixture primarily consisting of a stable blend of a film-forming polymer of monomers including at least a major proportion of vinyl chloride, a substantially non-volatile liquid phthalyl ester plasticizer amounting to 8 to 20 parts per 100 parts of said polymer, and a soft and viscous low-acid-number alkyd plasticizer resin in amount at least equal to the amount of said liquid phthalyl ester plasticizer, the total amount of said plasticizers being about ⅓ to ½ the amount of said polymer and the proportions being such that the adhesive tape has the properties of stretch and elasticity hereafter specified without causing pastiness or tack-loss of the contacting adhesive in the roll; and a eutohesive normally tacky and pressure-sensitive rubber-resin type adhesive coating united to the inner face of said film backing; said adhesive tape being unwindable without delamination or offsetting of adhesive, being originally stretchable by hand-pulling to an extent of at least 50% at room temperature and being substantially completely retractable from an elongation of 30% as herein specified.

2. An adhesive tape according to claim 1, wherein the adhesive includes a small proportion of an oil-soluble heat-reactive phenol-aldehyde resin.

3. An adhesive tape according to claim 1 in which the film-forming polymer is a copolymer of vinyl chloride and a minor proportion of vinyl acetate, said copolymer having a softening temperature of at least about 280° *F.* [C.].

4. A pressure-sensitive adhesive insulating tape wound upon itself in roll form and comprised of: (1) a stretchable and elastic film backing having a thickness of 4 to 10 mils and formed of a homogeneous mixture primarily consisting of a stable blend of 70 parts of a copolymer of vinyl chloride and a minor proportion of vinyl acetate, about 10 parts of a substantially non-volatile liquid phthalyl ester plasticiser, and about 20

parts of a soft and viscous low-acid-number alkyd plasticiser resin; (2) an adhesive primer coating on the inside face of the film backing adapted to increase the anchorage of the adhesive coating; and (3) a eucohesive normally tacky and pressure-sensitive rubber-resin type adhesive coating bonded to said primer coating; said adhesive tape being unwindable without delamination or offsetting of adhesive, being originally stretchable to an extent of at least 100% at room temperature and being substantially completely retractable from an elongation of 30% as herein specified.

5. An adhesive tape according to claim 4, wherein the adhesive includes a small proportion of an oil-soluble heat-reactive phenol-aldehyde resin.

6. A pressure-sensitive adhesive insulating tape wound upon itself in roll form and comprising: (1) a water-insoluble and hydrocarbon-oil-insoluble film backing of high dielectric strength containing a stabilizer and having a thickness of 4 to 20 mils and formed of a homogeneous mixture primarily consisting of a stable blend of (a) a film-forming polymer of monomers including at least a major proportion of vinyl chloride, and (b) a substantially non-volatile plasticizing material therefor in an amount within the range of at least ⅓ the weight of said polymer but in a substantially lesser amount than said polymer and comprising at least a major proportion of a non-migrating viscous plasticizer resin, and the proportions being such that the adhesive tape has the properties of stretch, elasticity and retractability hereafter specified without causing pastiness or loss of the tack of the contacting adhesive in the roll; (2) an adhesive primer coating on the inner face of the film backing adapted to increase the anchorage of the adhesive costing; and (3) a water-insoluble normally tacky and pressure-sensitive rubber-resin type adhesive coating united to the inner face of said film backing, over said primer coating, said adhesive coating being thin in relation to said film backing; said film backing being in permanent equilibrium with said pressure-sensitive adhesive coating so as to avoid pastiness or loss of tack of the said adhesive coating and diminution of the flexibility of said film backing; said adhesive tape being unwindable from the roll without delamination of the tape or offsetting of the adhesive, being originally stretchable in widths not greater than about one inch by simple hand pulling, exercising a force of not more than about 10 to 15 pounds, to an extent of at least 50% at room temperature and being substantially completely retractable from an elongation of 30%, as herein specified; said tape being readily conformable to irregular surfaces in insulating wire splices and its elasticity, retractability and high adhesion value making it easy, in insulated splices, to produce snug wrappings and coverings, and said tape having sufficiently aggressive adhesiveness to remain tightly and snugly wrapped around splices and wires.

7. A pressure-sensitive adhesive tape capable of being wound upon itself in roll form and unwound therefrom without delamination or offsetting of the adhesive and comprising a water-insoluble and hydrocarbon-oil-insoluble film backing having a thickness of about 4 to 20 mils and formed of a homogeneous mixture primarily consisting of a stable blend of (a) a film-forming polymer of monomer material including at least a major proportion of vinyl chloride, and (b) a

substantially non-volatile plasticizing material therefor in an amount within the range of at least about ⅓ the weight of said polymer but in a substantially lesser amount than said polymer and comprising at least a major proportion of a non-migrating viscous plasticizer, and the proportions being such that the adhesive tape has the properties of stretch, elasticity and retractability hereafter specified without causing pastiness or loss of the tack of the contacting adhesive; and a water-insoluble normally tacky and pressure-sensitive rubber-resin type adhesive coating united and firmly bonded to one face of said film backing; said film backing being in permanent equilibrium with said pressure-sensitive adhesive coating, so as to avoid pastiness or loss of the tack of said adhesive coating and loss of the flexibility of said film backing; said adhesive tape being capable of being wound upon itself in roll form and unwound therefrom without delamination of the tape or offsetting of the adhesive, being originally stretchable in widths not greater than about one inch by simple hand pulling, exercising a force of not more than about 10 to 15 pounds, to an extent of at least 50% at room temperature and being substantially completely retractable from an elongation of 30%, as herein specified; said tape being readily conformable to irregular surfaces and its elasticity, retractability and high adhesion value making it easy to produce snug, smooth-fitting wrappings and coverings.

8. A pressure-sensitive adhesive tape capable of being wound upon itself in roll form and unwound therefrom without delamination or offsetting of the adhesive and comprising a water-insoluble and hydrocarbon-oil-insoluble film backing having a thickness of about 4 to 20 mils and formed of a homogeneous mixture primarily consisting of a stable blend of (a) a film-forming polymer of monomer material including at least a major proportion of vinyl chloride, and (b) a substantially non-volatile plasticizing material therefor in an amount within the range of at least about ⅓ the weight of said polymer but not greatly in excess of ½ the weight of said polymer and comprising at least a major proportion of a non-migrating viscous plasticizer resin, and the proportions of the said plasticizing material to said film-forming polymer being such that the adhesive tape has the properties of stretch, elasticity and retractability hereafter specified without causing pastiness or loss of the tack of the contacting adhesive; and a water-insoluble, normally tacky and pressure-sensitive rubber resin type adhesive coating united and firmly bonded to one face of said film backing, said adhesive coating being thin in relation to said film backing; said film backing being in permanent equilibrium with said pressure-sensitive adhesive coating, so as to avoid pastiness or loss of the tack of said adhesive coating and loss of the flexibility of said film backing; said adhesive tape being capable of being wound upon itself in roll form and unwound therefrom without delamination of the tape or offsetting of the adhesive, being originally stretchable in widths not greater than about one inch by simple hand pulling, exercising a force of not more than about 10 to 15 pounds, to an extent of at least 50% at room temperature and being substantially completely retractable from an elongation of 30%, as herein specified; said tape being readily conformable to irregular surfaces and its elasticity, retractability and high adhesion value making it easy to produce snug, smooth-fitting wrappings and coverings.

9. A pressure-sensitive adhesive insulating tape wound upon itself in roll form and comprising: (1) a water-insoluble and hydrocarbon oil-insoluble opaque pigmented film backing of high dielectric strength and having a thickness of about 4 to 12 mils and formed of a homogeneous mixture primarily consisting of a stable blend of (a) a film-forming polymer of monomers including at least a major proportion of vinyl chloride, and (b) a substantially non-volatile plasticizing material therefor in an amount within the range of at least about ⅓ the weight of said polymer but not in excess of about ½ the weight of said polymer and comprising at least a major proportion of a non-migrating viscous plasticizer resin, and the proportions of said plasticizing material to said film-forming polymer being such that the adhesive tape has the properties of stretch, elasticity and retractability hereafter specified without causing pastiness or loss of the tack of the contacting adhesive in the roll; (2) an adhesive primer coating on said film backing so as to increase the anchorage of the adhesive coating to the inner face of its backing when unwound from rolls thereof; and (3) a water-insoluble normally tacky and pressure-sensitive rubber resin type adhesive coating united to the inner face of said film backing, said adhesive coating being thin in relation to said film backing; said film backing being in permanent equilibrium with said pressure-sensitive adhesive coating so as to avoid pastiness or loss of the tack of the said adhesive coating and diminution of the flexibility of said film backing; said adhesive tape being unwindable from the roll without delamination of the tape or offsetting of the adhesive, being originally stretchable in widths not greater than about one inch by simple hand pulling, exercising a force of not more than about 10 to 15 pounds, to an extent of at least 50% at room temperature and being substantially completely retractable from an elongation of 30%, as herein specified; said tape being readily conformable to irregular surfaces in insulating wire splices and its elasticity, retractability and high adhesion value making it easy, in insulated splices, to produce snug wrappings and coverings, and said tape having sufficiently aggressive adhesiveness to remain tightly and snugly wrapped around splices and wires.

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